Femtochemistry Bonding and Dynamics with X-ray Free-Electron Lasers

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School on Synchrotron and Free-Electron-Laser Methods for Multidisciplinary Applications, ICTP (International Center for Theoretical Physics), Trieste (Italy), May 2018

Outline

1. **“I think I need to tell you why…”**
2. Setting the stage
3. Some basics
4. Methods
5. One application
6. One of many possible outlooks

Ever increasing demand for energy

Quantity (world)	2001	2050	2100
Energy consumption rate TW	13.5	27.6	43.0
Population billion persons	6.1	9.4	10.4
Gross domestic product $/person·year	7470	14850	27320

- Electricity
- Heat
- Fuels

- Secure
- Clean
- Sustainable

- Make
- Store, transport
- Release

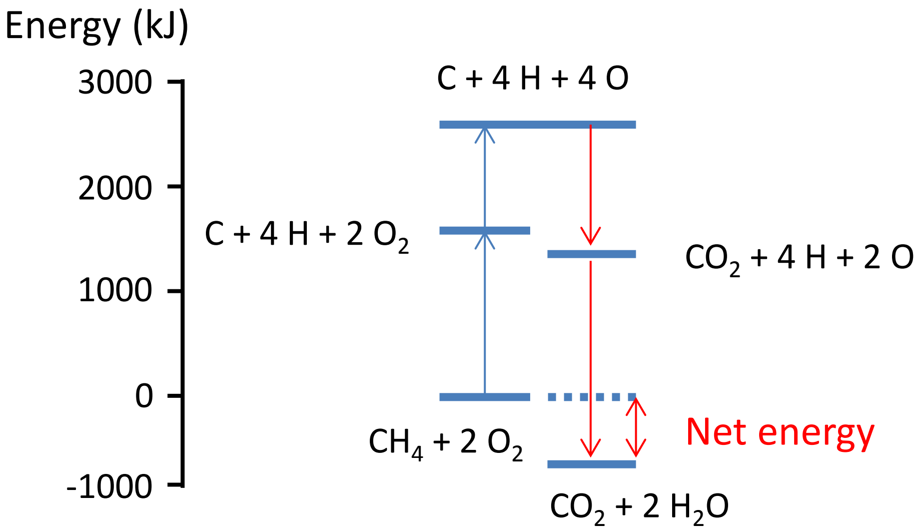
Lewis, Nocera, PNAS **103**, 15729 (2006)
Lubitz, Reijerse, Messinger, Energy Environ. Sci. **1**, 15 (2008)

Energy and chemical bonds

Material	Energy type	Specific energy* (MJ/Kg)
Uranium	Fission	80620000
Hydrogen (700 bar)	Chemical	142
Kerosene	Chemical	42.8
Lithium-ion battery	Electrochemical	0.5

* Measured as thermal energy (amount of heat energy that can be extracted)

Combustion of methane to CO_2, water and heat

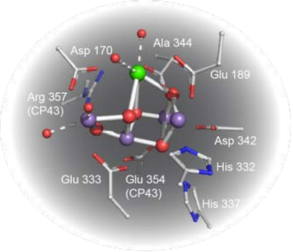


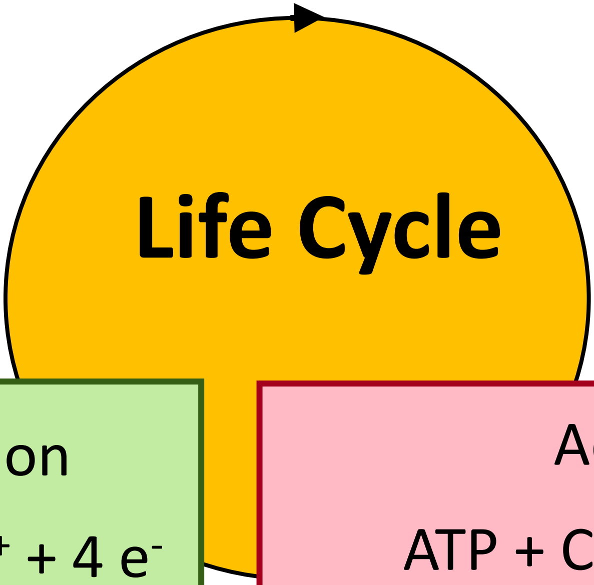
https://en.wikipedia.org/wiki/Energy_density#Energy_storage

Photosynthesis

$$CO_2 + H_2O \xrightarrow{\hbar\omega} (CH_2O)_n + O_2$$

This process generates carbohydrates and the world supply of oxygen





Life Cycle

Photosystem II

How?

Oxygen evolution

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$$

The oxygen is derived from water

Cytochrome Oxidase

Aerobic metabolism

$$ATP + CO_2 + H_2O \leftarrow (CH_2O)_n + O_2$$

We consume oxygen to “burn” the energy of carbohydrates to produce ATP, the biological energy currency

Suga et al., Nature **517**, 99 (2015), Young et al., Nature **540**, 453 (2016), Kupitz et al., Nature **513**, 261(2014)

Water splitting – Rearranging bonds

$2\,H_2O \longrightarrow 2\,H_2 + O_2$ **Energy = 237 kJ/mol, 13 million J/liter**

Piscina Agonistica Comunale Bruno Bianchi Trieste

Approx. 50 m x 15 m x 2 m
1.5 million liters of water

Water in *Piscina Agonistica Comunale Bruno Bianchi Trieste* split every second = 19.5 TW

World consumption rate in 2001 = 13.5 TW

Recreating the life cycle

Artificial Photosynthesis

$$CO_2 + H_2O \xrightarrow{\hbar\omega} \text{Fuel } (H_2, CH_4, CH_3OH, \ldots) + O_2$$

$$\text{Fuel} + O_2 \rightarrow CO_2 + H_2O$$

JCAP*: "Discover new ways to produce hydrogen and carbon-based fuels using only sunlight, water and carbon dioxide as inputs…"

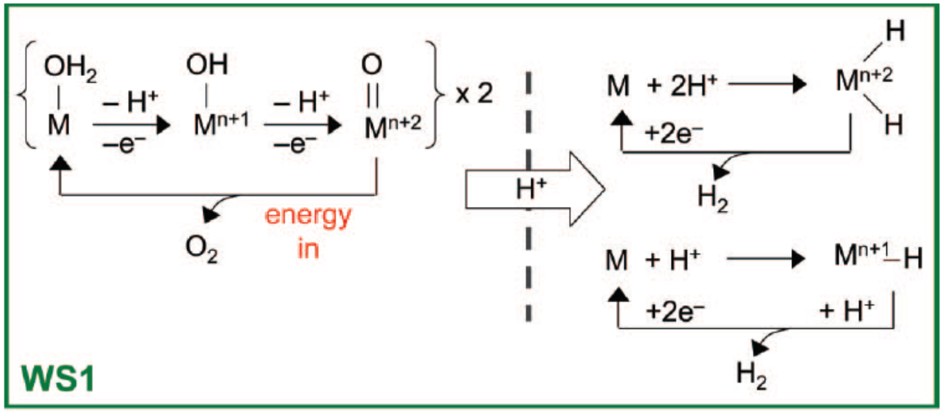
Lewis, Nocera, PNAS **103**, 15729 (2006)
Lubitz, Reijerse, Messinger, Energy Environ. Sci. **1**, 15 (2008)

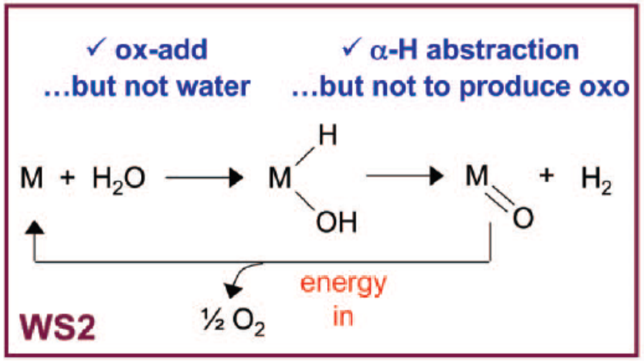
*www.solarfuelshub.org

Engineering chemical bonds

Nocera: „Unexplored basic science issues are immediately confronted when the problem is posed in the simplest chemistry framework.“

Water splitting stategies





Lewis, Nocera, PNAS **103**, 15729 (2006)

Learn to rearrange bonds

Characterize molecules in weird bonding configurations

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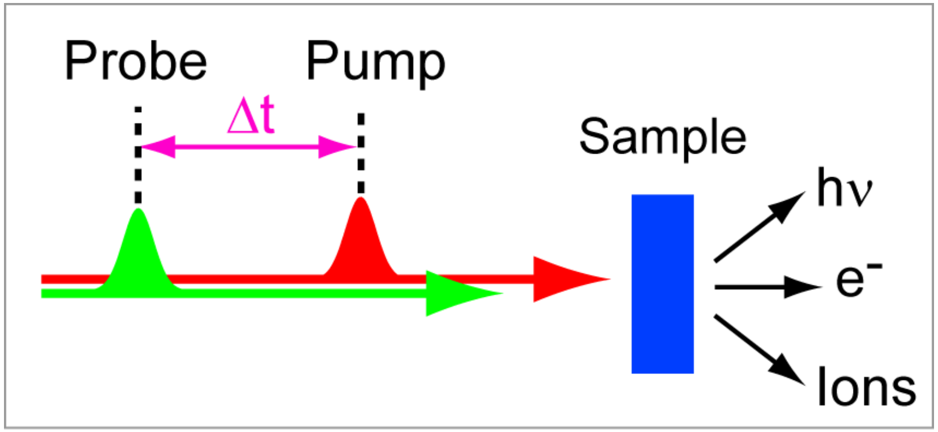
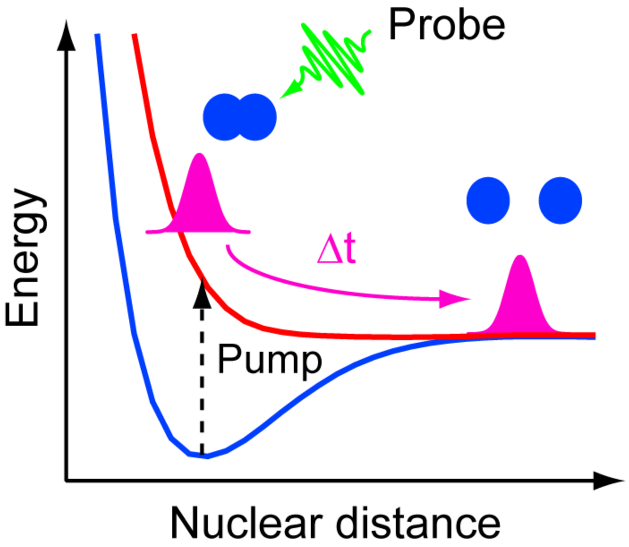
Pump-probe spectroscopy





Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

Outline

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What time-resolution do I need to resolve molecular motion?

Take the speed of sound

- Resolve corresponding displacements
- “Speed of atoms” several 100-1000 m/s
- This corresponds to resolving 100-1000·10^{10} Å/10^{15} fs = 0.1-1 Å/100 fs

What time-resolution do I need to resolve molecular motion?

Take the oscillation period of a molecule

- Resolve the oscillatory motion
- E.g. 3500 cm^{-1} (wavelength of ~3 µm) for the O-H stretch vibration in H_2O
- $T = 1/f$, $c=\lambda\cdot f \rightarrow T = \lambda/c \rightarrow T = 3\cdot10^{-6}m/(3\cdot10^{8}m/s) = 10^{-14}\,s$
- This corresponds to a duration of the vibrational period of ~10 fs

What time-resolution do I need to resolve molecular motion?

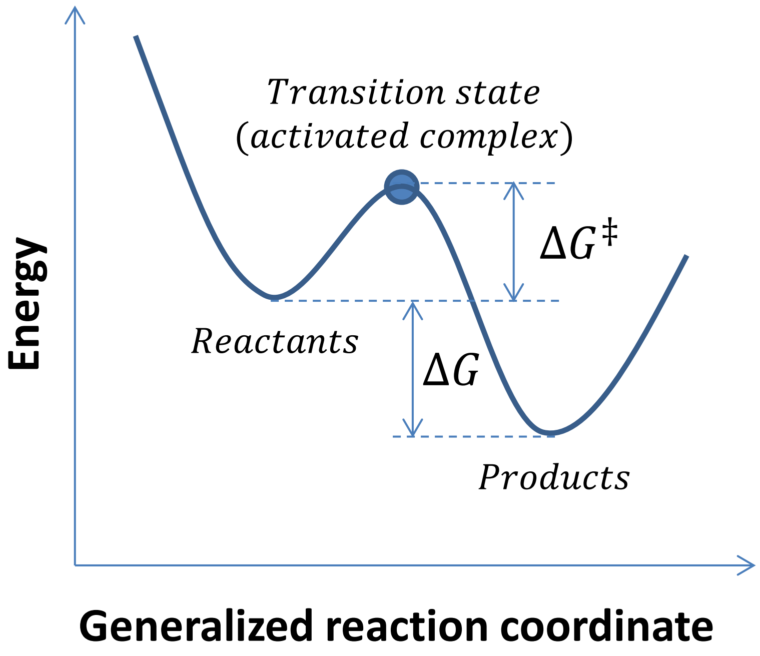
Take the Brownian motion

- Resolve the mean square displacement $x^2(t)$ with time t: $x^2(t) = \frac{k_B T}{3\pi R \eta} t$
- With T temperature, R particle radius, η viscosity
- Albert Einstein (1905), Marian Smoluchowski (1906) and Paul Langevin (1908)
- Displacement of 1 Å takes 100 fs (R = 1 Å, $\eta = 20 \cdot 10^{-6}$ kg/(m·s) for O_2, ideal gas)

Wait a second: What do we actually talk about?

Chemical dynamics deals with the atomic-scale view of the elementary steps of a chemical reaction (pico- to femtoseconds and Ångstrom).

This could be a triggered reaction (pump-probe) or a non triggered reaction (e.g. thermally activated). Most often, photoreactions (triggered) are studied!



Thermodynamics

$$K = \frac{[Products]}{[Reactants]} = e^{-\frac{\Delta G}{RT}}$$

Transition state theory

$$k = \upsilon \cdot e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

- Thermodynamic properties of the transition state ($\Delta G^{\ddagger}$) and the crossing frequency (υ) determine the reaction rate (k) (the kinetics) of thermal reactions (equilibrium)
- The energy potential landscapes determine the reaction mechanisms (the dynamics) of photochemical reactions

We talk about the atomic-scale dynamics of chemical interactions

See extra slides on the delineation of kinetics and dynamics!

The Born-Oppenheimer Approximation

- When we describe chemical interactions
- By forming molecular from atomic orbitals
- We often assume the nuclei to be at rest
- We need to drop this approximation!
- Nuclear movements are now part of the problem!
- This problem is not analytically solvable…
- We need the Born-Oppenheimer approximation!

Max Born and Robert Oppenheimer: **Zur Quantentheorie der Molekeln**, *Annalen der Physik*, **389** (20), p. 457–484 (1927).

The Born-Oppenheimer Approximation

By neglecting the coupling of nuclear and electron motions we can treat the motion of nuclei and electrons independently.

Masses of electrons and nuclei are so different (10^4) **that the nuclei appear to be fixed while electrons are moving!**

Solve the Schrödinger equation for the **electrons in the static potential of the fixed nuclei** ("Produktansatz").

The electronic part of the wavefunction depends on the nuclear coordinates BUT as a parameter, NOT as a variable!

$$\boxed{\begin{gathered}\Psi_{\text{molecule}} = \Psi_e \cdot \Psi_n \\ \Psi_e = \Psi_e(r_e, R_n) \\ \Psi_n = \Psi_n(R_n)\end{gathered}}$$

Within the adiabatic approximation ("electrons follow nuclear motions instantaneously") we can solve the Schrödinger equation for Ψ_e at fixed R_n repeatedly for many R_n:

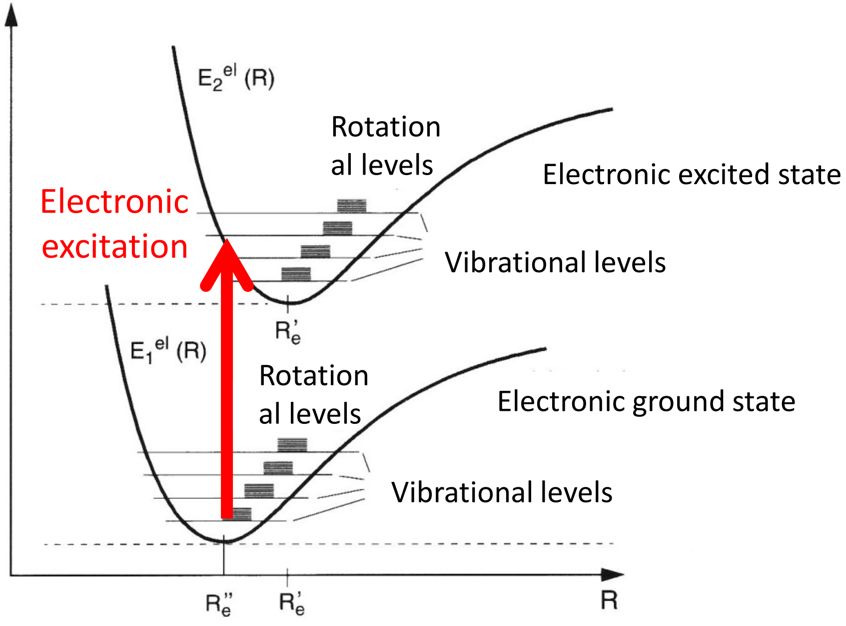
$$[T_e + V_e]\ \Psi_e(r_e, R_n=\text{const}) = E_e\ \Psi_e(r_e, R_n=\text{const})$$

T_e/V_e = kinetic/potential energy of electrons

By plotting the resulting set of solutions E_e versus R_n we build potential energy curves!

(surfaces, landscapes, depending on the number of parameters/reaction coordinates)

The Born-Oppenheimer Approximation



The potential energy curve E_e versus R_n corresponds to the "electronic part" of the total energy of the molecules plus the energy arising from repulsion of the nuclei (sum of kinetic and potential energy of electrons plus potential energy of nuclei)

Vibrational and rotational energies of the molecule are missing!

Demtröder, Molekülphysik

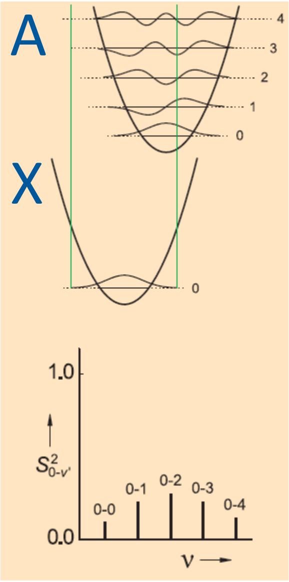
The Franck-Condon Principle

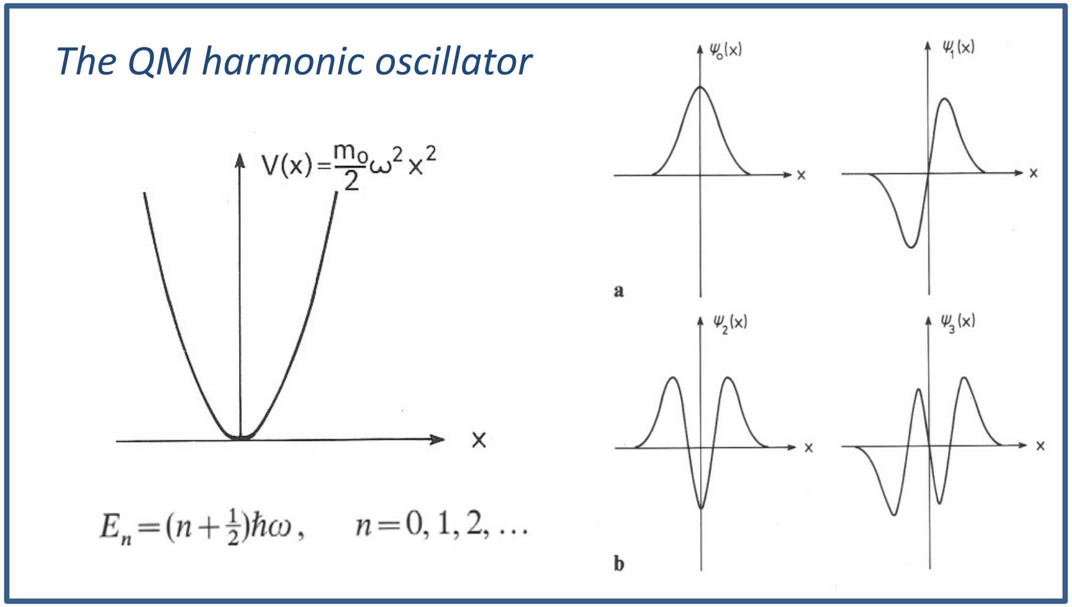
For the transition between state X and A with vibrational levels υ the transition probability (electronic dipole transition) is proportional to:

The **electronic dipole moment** times the **Franck-Condon factors**

$$|\langle \Psi_e^A \mid d_e \mid \Psi_e^X \rangle|^2 \qquad \cdot \qquad |\langle \Psi_n^\upsilon \mid \Psi_n^0 \rangle|^2$$

$$\left|\int \Psi_e^A \; d_e \; \Psi_e^X \; dr_e\right|^2 \qquad \cdot \qquad \left|\int \Psi_n^\upsilon \, \Psi_n^0 \, dR_n\right|^2$$

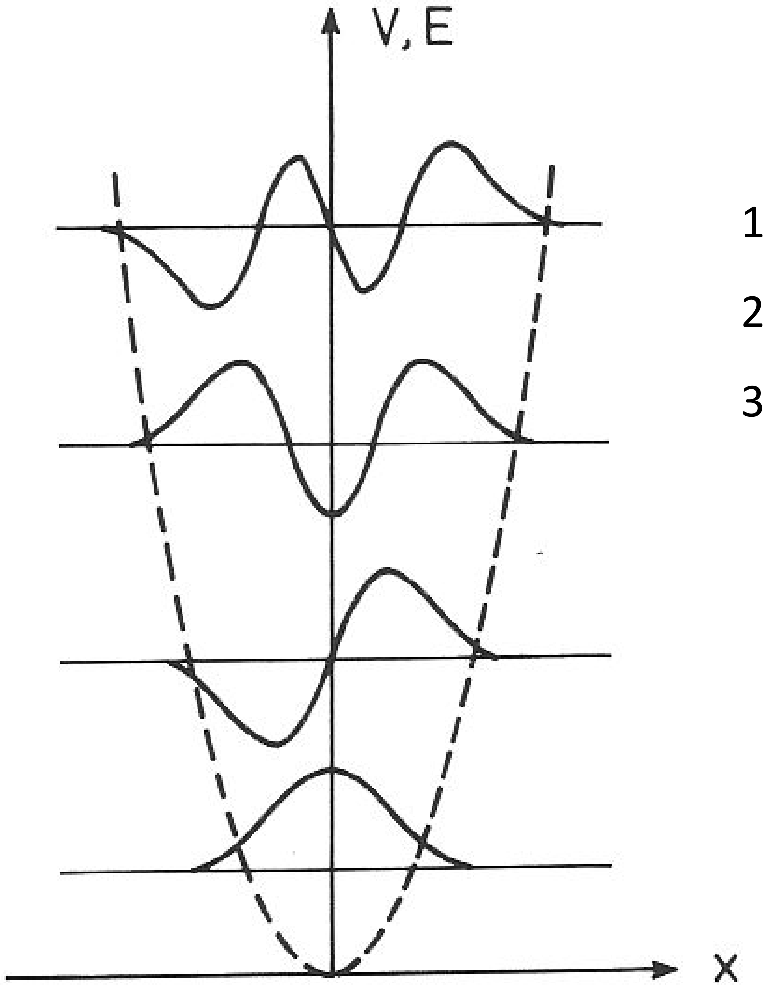



The QM harmonic oscillator

$$E_n=(n+\tfrac{1}{2})\hbar\omega\,, \qquad n=0,1,2,\dots$$

Haken/Wolf *Molecular Physics and Elements of Quantum Chemistry*
Atkins/Friedman *Molecular Quantum Mechanics*

How many drawings in one?



1. Shape of the harmonic potential V(x)
2. Energy levels E of the harmonic oscillator
3. Nuclear wavefunctions plotted vs. x

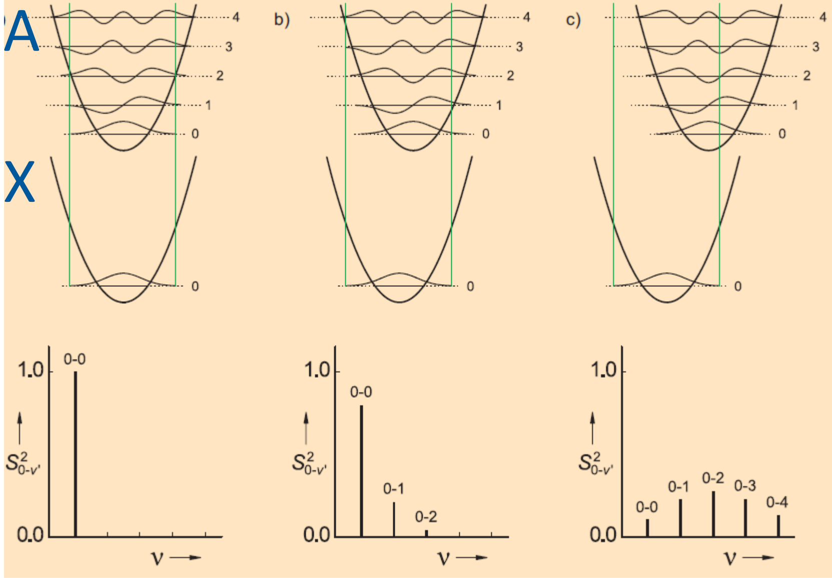
The Franck-Condon Principle

For the transition between state X and A with vibrational levels υ the transition probability (electronic dipole transition) is proportional to:

The **electronic dipole moment** times the **Franck-Condon factors**

$$|< \Psi_e^A \mid d_e \mid \Psi_e^X > |^2 \qquad \cdot \qquad |< \Psi_n^\upsilon \mid \Psi_n^0 > |^2$$

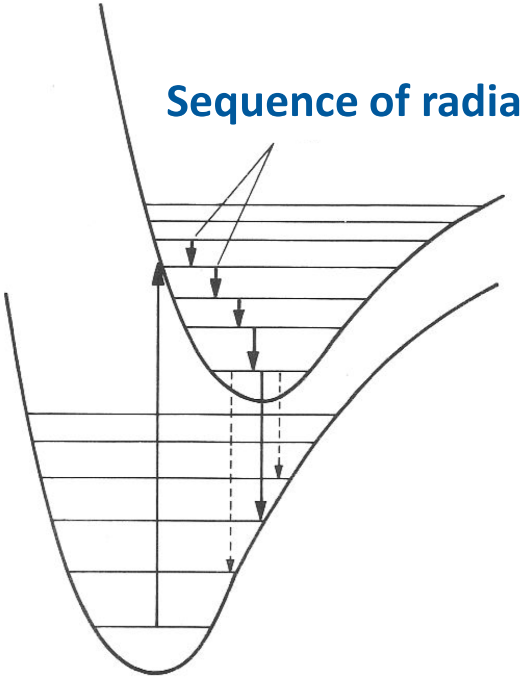
$$|\int \Psi_e^A \; d_e \, \Psi_e^X \; dr_e|^2 \qquad \cdot \qquad |\int \Psi_n^\upsilon \, \Psi_n^0 \, dR_n|^2$$



Those overlap integrals *S* are the famous **Franck-Condon factors**

Haken/Wolf *Molecular Physics and Elements of Quantum Chemistry*
Atkins/Friedman *Molecular Quantum Mechanics*

Electronic excitation and (ultrafast) relaxation

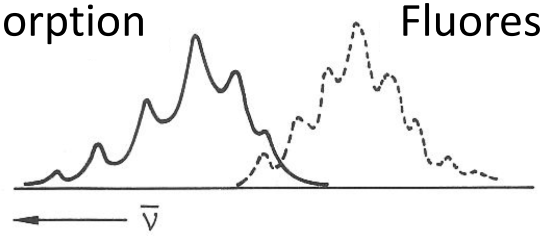


Sequence of radiationless transitions

- Internal conversion
- Intramolecular vibrational redistribution
- Intersystem crossing
- Thermalization

(see extra slides for details)

Absorption Fluorescence



Red-shift of fluorescence!

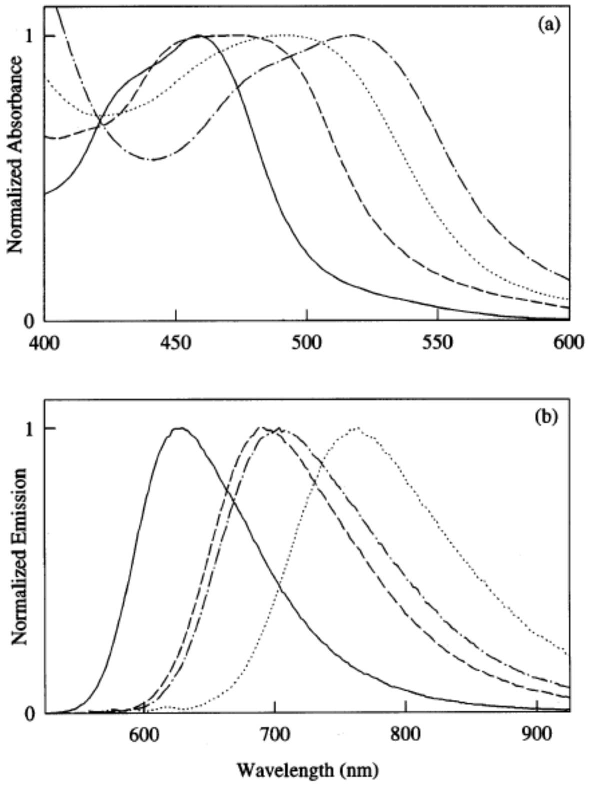
Haken/Wolf *Molecular Physics and Elements of Quantum Chemistry*

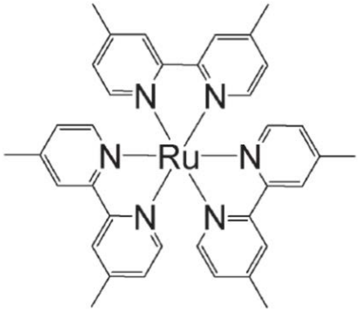
Electronic excitation and (ultrafast) relaxation

A famous example

Absorption

Fluorescence
(Emission)





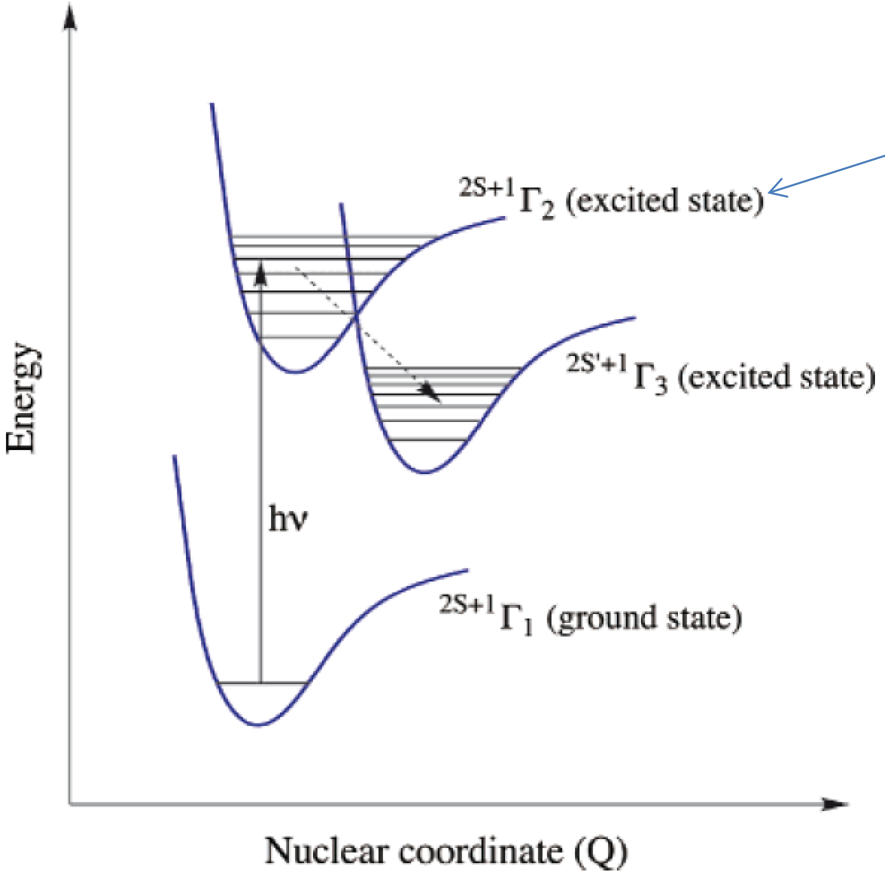
Wai-Yeung Wong (Ed.)
Organometallics and Related Molecules for Energy Conversion

FIGURE 4. (a) Electronic absorption spectra of [Ru(dmb)$_3$]$^{2+}$ (—), [Ru(dmb)$_2$(dea)]$^{2+}$ (- - -), [Ru(dmb)(dea)$_2$]$^{2+}$ (•••), and [Ru(dea)$_3$]$^{2+}$ (- • -), all in CH$_3$CN solution. (b) Static room-temperature emission spectra for [Ru(dmb)$_3$]$^{2+}$ (—), [Ru(dmb)$_2$(dea)]$^{2+}$ (- - -), [Ru(dmb)(dea)$_2$]$^{2+}$ (•••), and [Ru(dea)$_3$]$^{2+}$ (- • -), all in deoxygenated CH$_3$CN solution. (Adapted from ref 18.)

Femtosecond Absorption Spectroscopy of Transition Metal Charge-Transfer Complexes, James K. McCusker, Acc. Chem. Res. **36**, 876-887 (2003).

Electronic excitation and (ultrafast) relaxation

A famous example



If we can make this state live long, we can efficiently make use of the electron-hole pair!

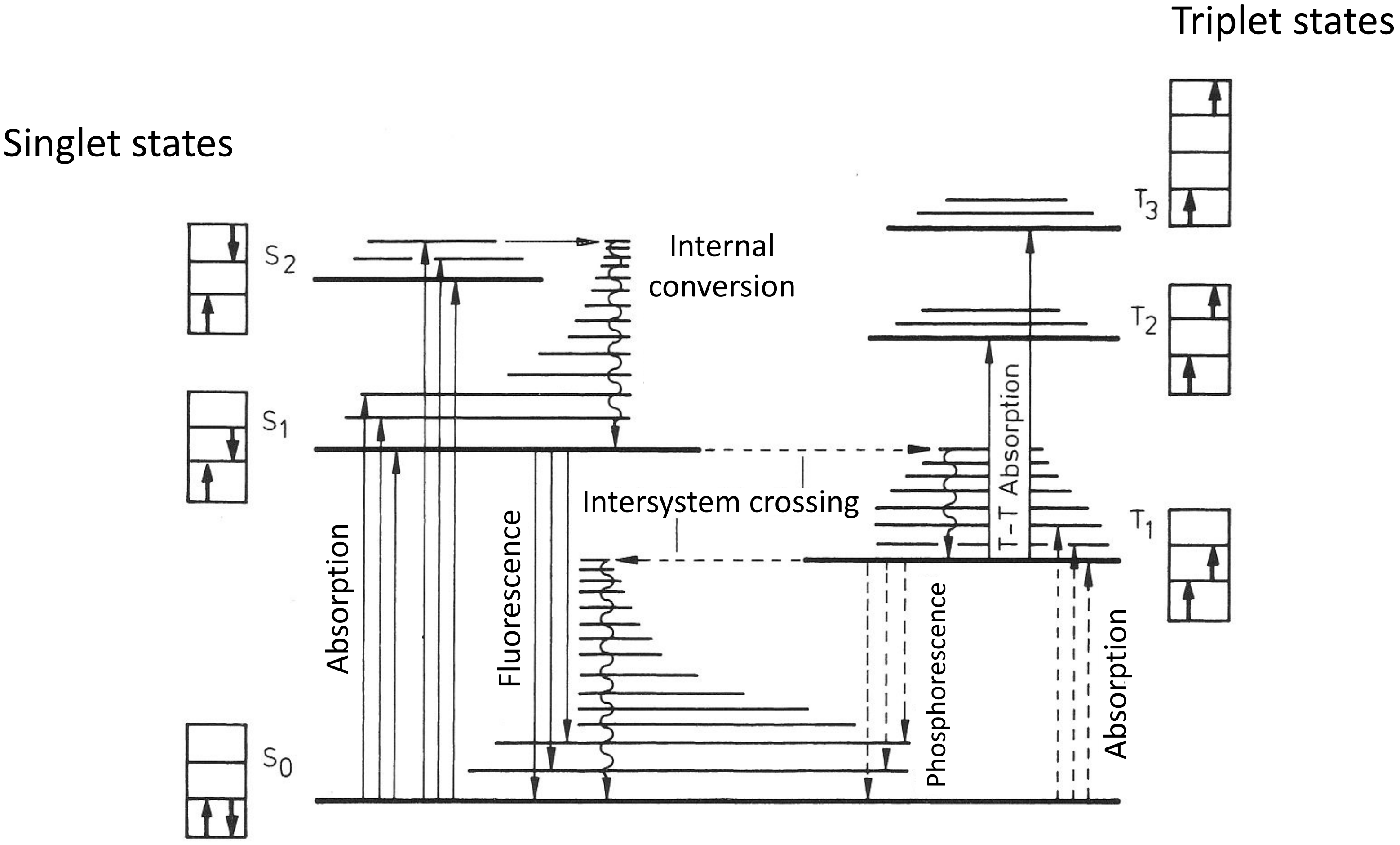
Charge separation
→ Henrik Lemkes lecture!

FIGURE 1. Generalized potential energy surface diagram for excited-state evolution. Initial excitation from the ground state ($^{2S+1}\Gamma_1$, where *S* denotes the spin state) to the higher-lying excited state ($^{2S+1}\Gamma_2$) is followed by relaxation to the lower-energy surface ($^{2S'+1}\Gamma_3$). Understanding the dynamics and mechanism of the $^{2S+1}\Gamma_2 \rightarrow {}^{2S'+1}\Gamma_3$ conversion as it occurs in transition-metal charge-transfer complexes is the focus of the research described in this Account.

Femtosecond Absorption Spectroscopy of Transition Metal Charge-Transfer Complexes, James K. McCusker, Acc. Chem. Res. **36**, 876-887 (2003).

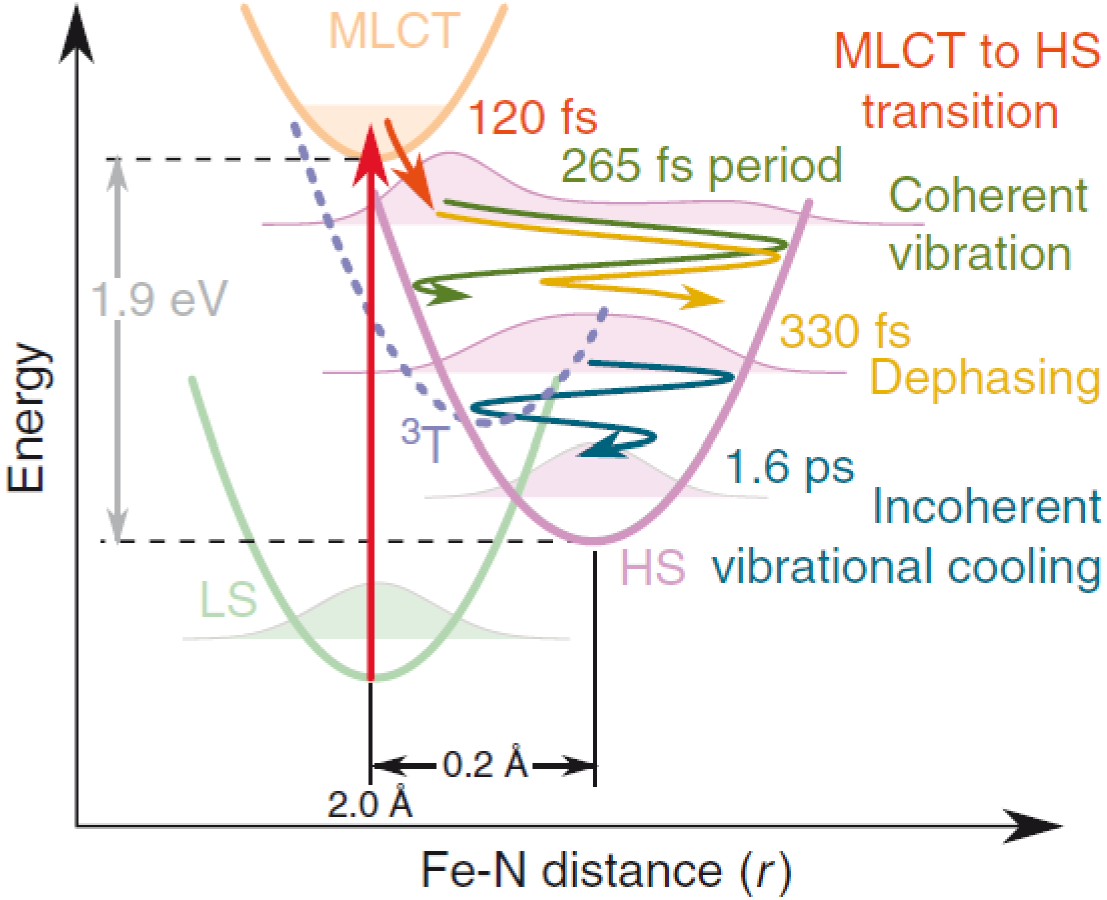
Electronic excitation and (ultrafast) relaxation

Typical state energy diagram of a molecule



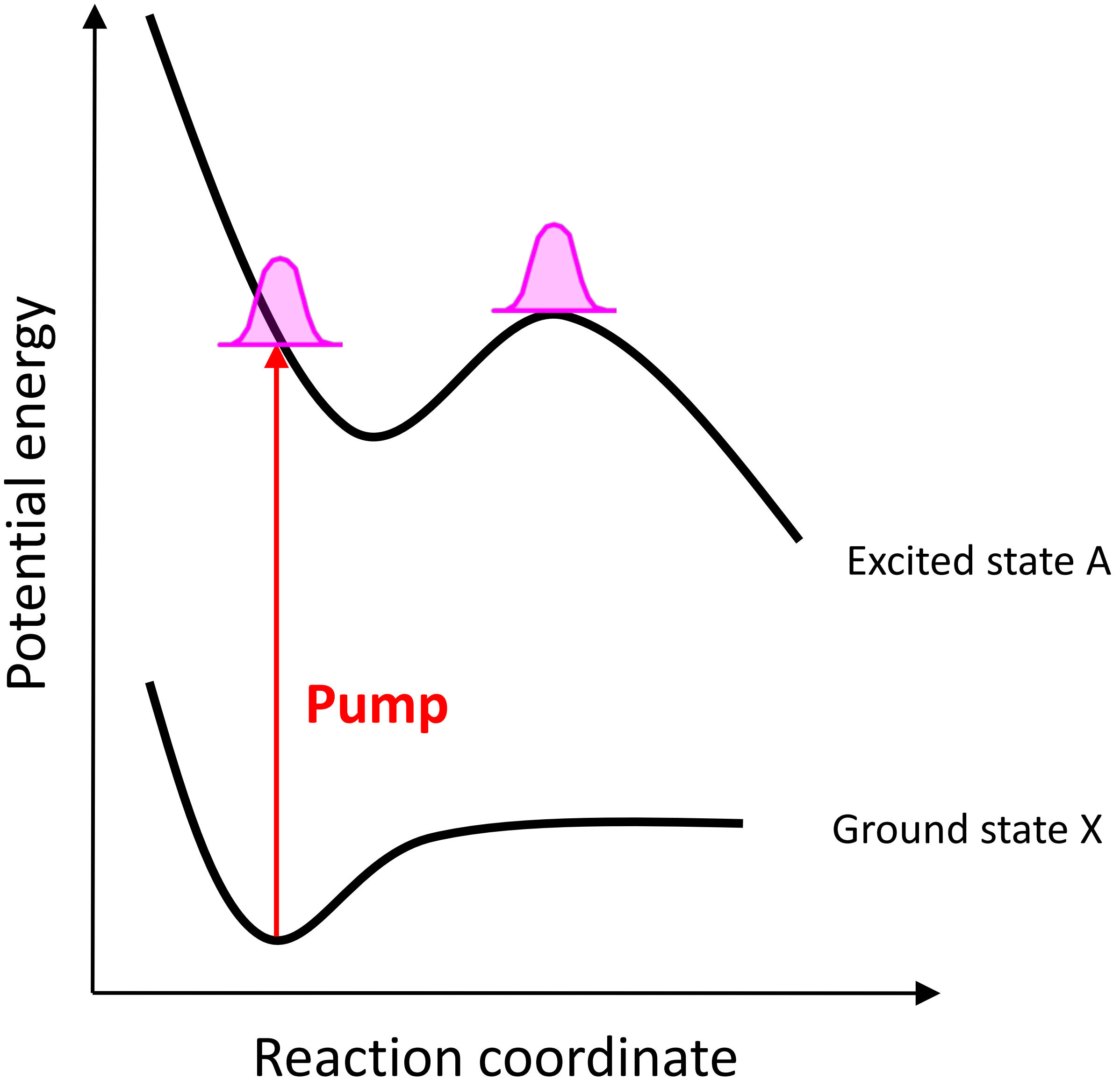
Haken/Wolf *Molecular Physics and Elements of Quantum Chemistry*

Electronic excitation and (ultrafast) relaxation

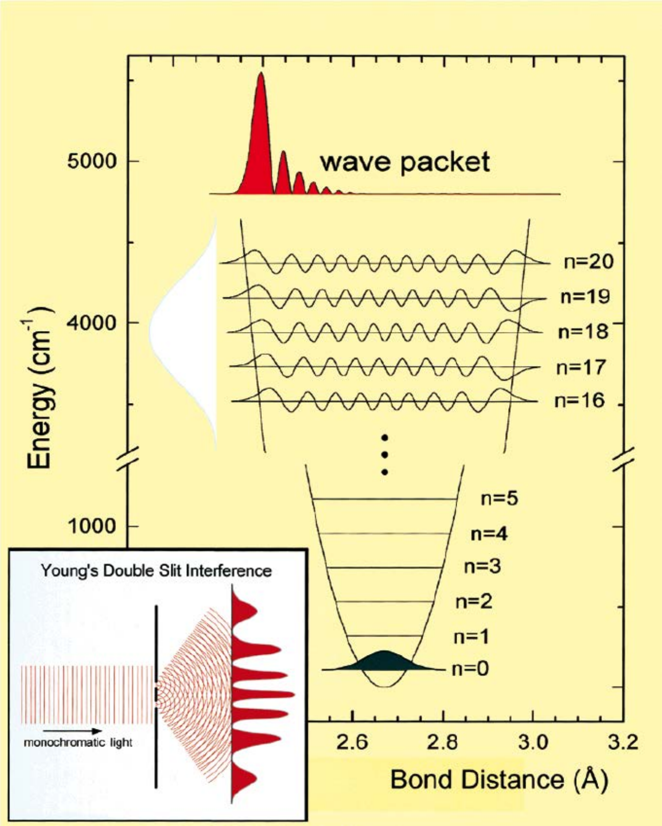


H. Lemke at al., Nature Communications **8**, 15342 (2017).

Describing nuclear motion



(Nuclear) Wavepackets



A. Zewail

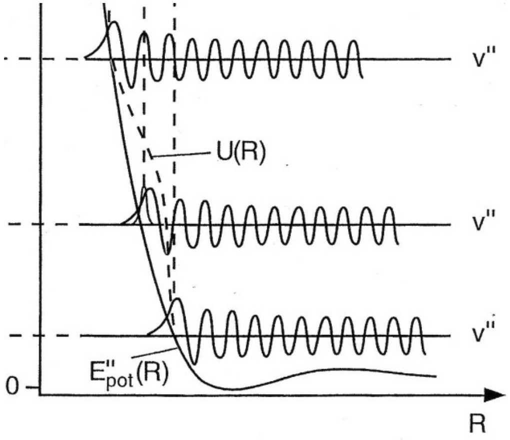
J. Phys. Chem. A **2000**, *104*, 5660−5694

- Coherent superposition of vibrational states
- Formation of a nuclear wavepacket
- The wavepacket is evolving in time (nuclei are moving)!
- Wavepackets to describe particles confined in space

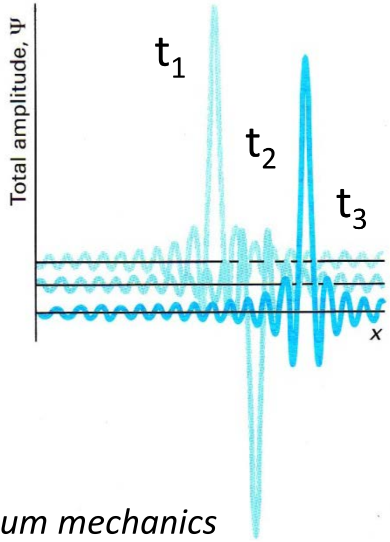
Superposing plane waves

$$\Psi(x,\, t) = (2\pi\hbar)^{-1/2}\int_{-\infty}^{+\infty} e^{i(p_x x - Et)/\hbar}\,\phi(p_x)\, dp_x$$

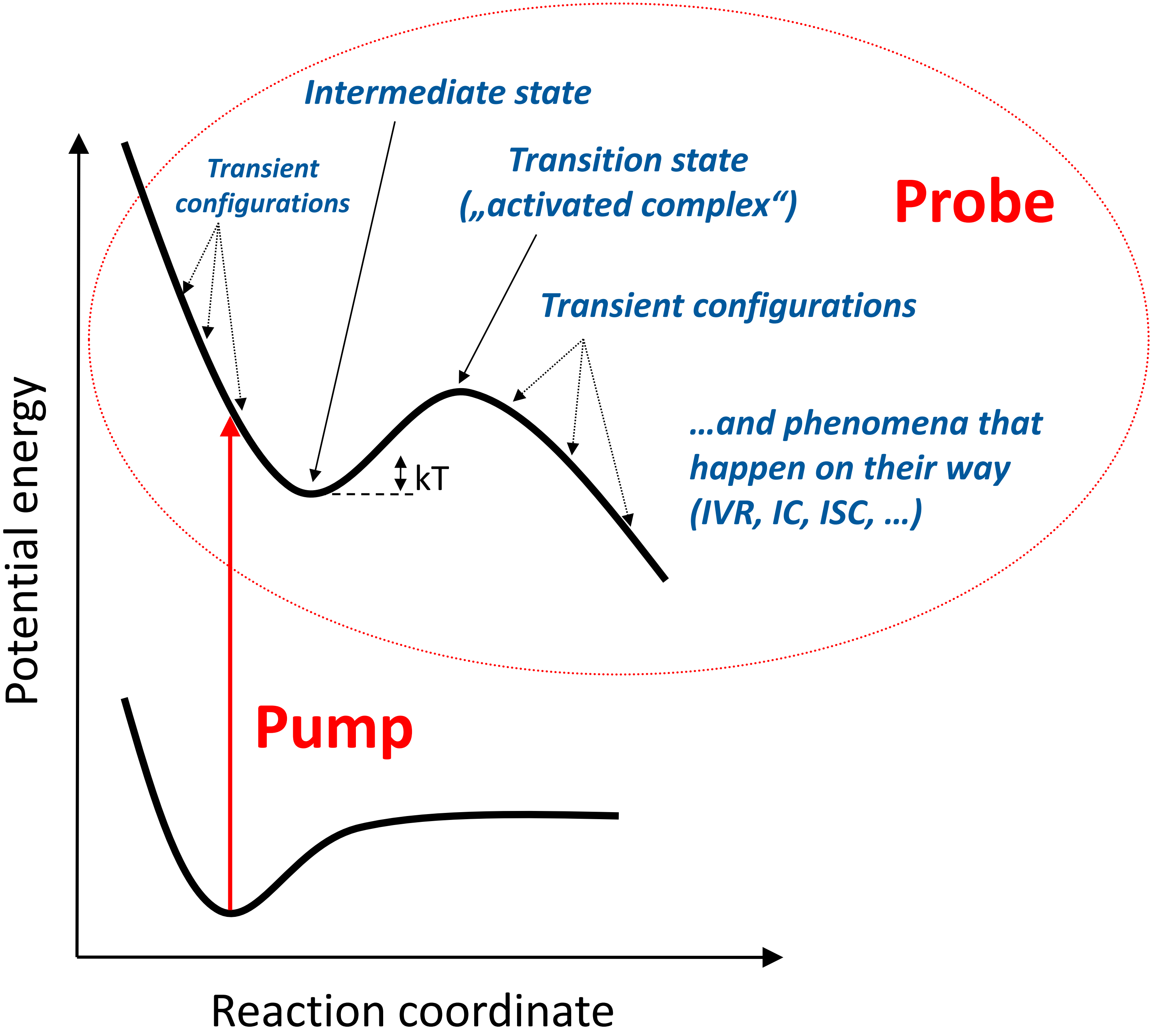
For dissociative states



For free particles



Atkins, Friedman, Molecular quantum mechanics



Intermediate state

Transient configurations

Transition state („activated complex“)

Probe

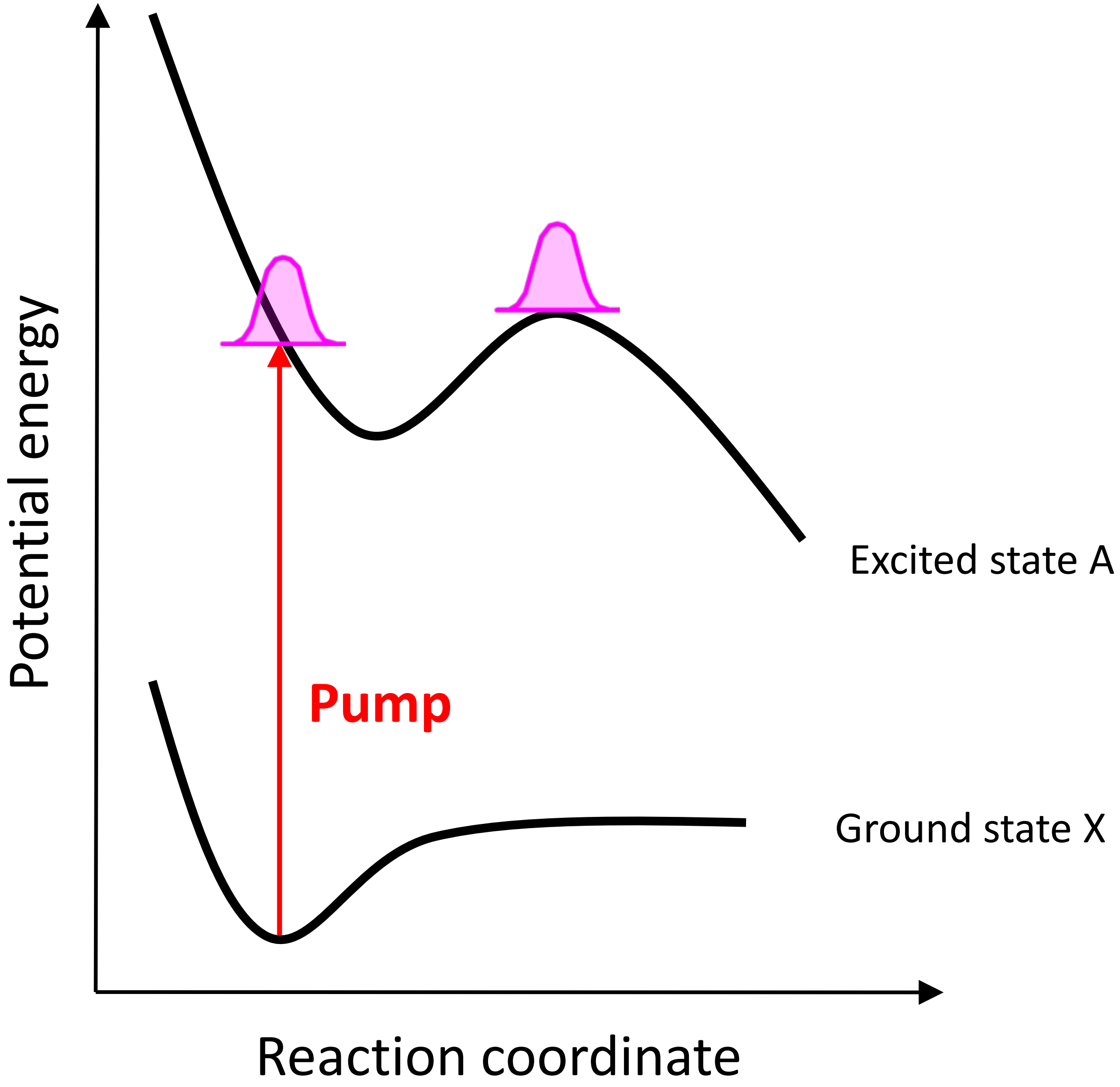
Transient configurations

…and phenomena that happen on their way (IVR, IC, ISC, …)

kT

Pump

What is “wrong” here (within the BOA)?



Beyond the Born-Oppenheimer Approximation

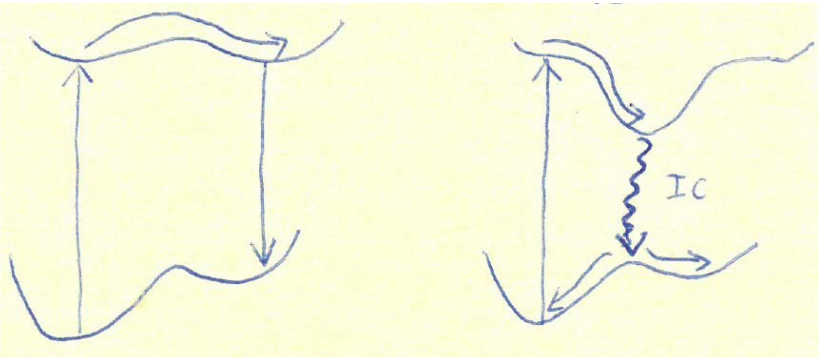
Getting from one state to another via Conical Intersections (CI)

Adiabatic
No exchange of energy

Non-adiabatic
With exchange of energy

Excited state

Ground state



Excited and ground states couple non-adiabatically enabling non-radiative transitions

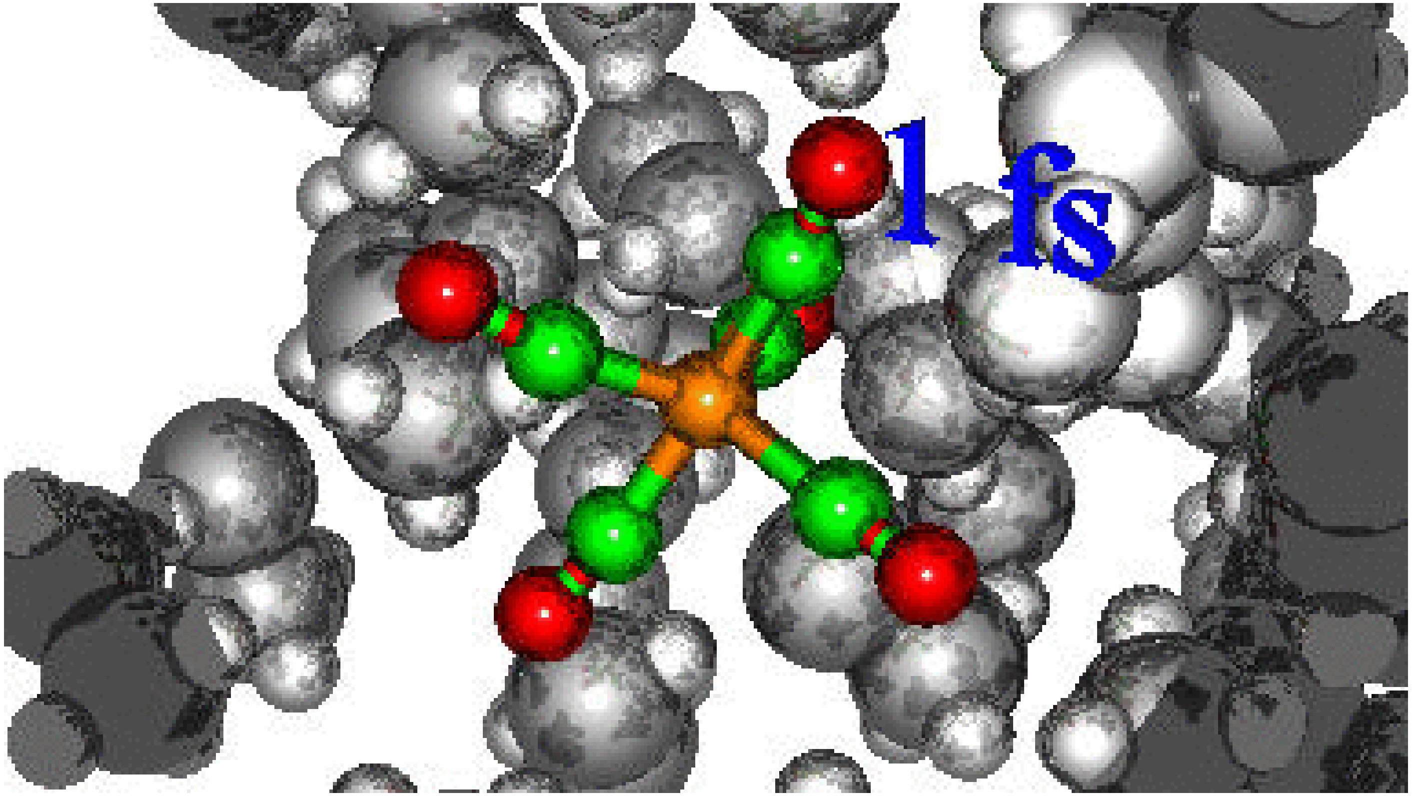
Born-Oppenheimer approximation: Nuclei move on adiabatic potential energy surfaces

- CIs = Points/seams where potential energy surfaces are degenerate (intersect)
- At CIs states states couple non-adiabatically, BOA breaks down, coupled electron-nuclear dynamics, non-adiabatic processes (e.g. Internal Conversion, IC) take place
- Nuclear motion around the CI = Non-radiative (highly efficient) transitions between states become possible
- Ultrafast atomic motion otherwise inaccessible (in excited and ground states)

→ CIs play major roles in photochemical reactions and ultrafast radiationless decays. Ultrafast atomic movements can then lead to unique electronic properties!

What do you see?

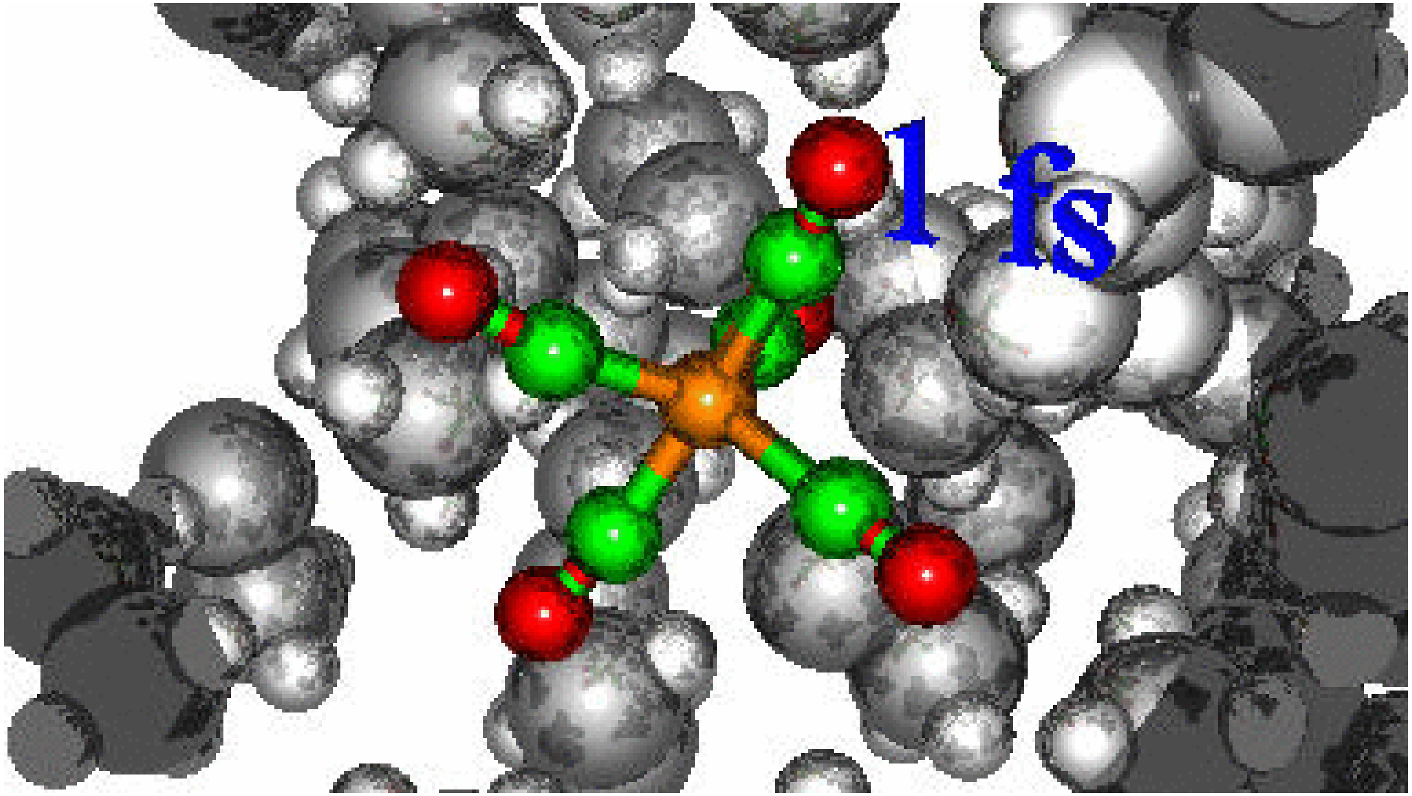
Molecular dynamics simulation
Michael Odelius (Stockholm University)



$Fe(CO)_5$ dissociation in ethanol

Where are the electrons?

Molecular dynamics simulation
Michael Odelius (Stockholm University)



$Fe(CO)_5$ dissociation in ethanol

How fast do electrons move?

- Ask yourself: Why do I care?
- Do I want to observe electron motion?
- Do I want to follow the rearrangements of electrons as nuclei are moving?
  - **I need fs time resolution!**

- So what time resolution do I need to observe electron motion?

How fast do electrons move?

Take the most basic atom and look at the electron in the ground state of the atom

- Classically the electron takes 150 as to circulate the proton
- I need as temporal resolution

How fast do electrons move?

Take a scattering approach and the Heisenberg uncertainty principle

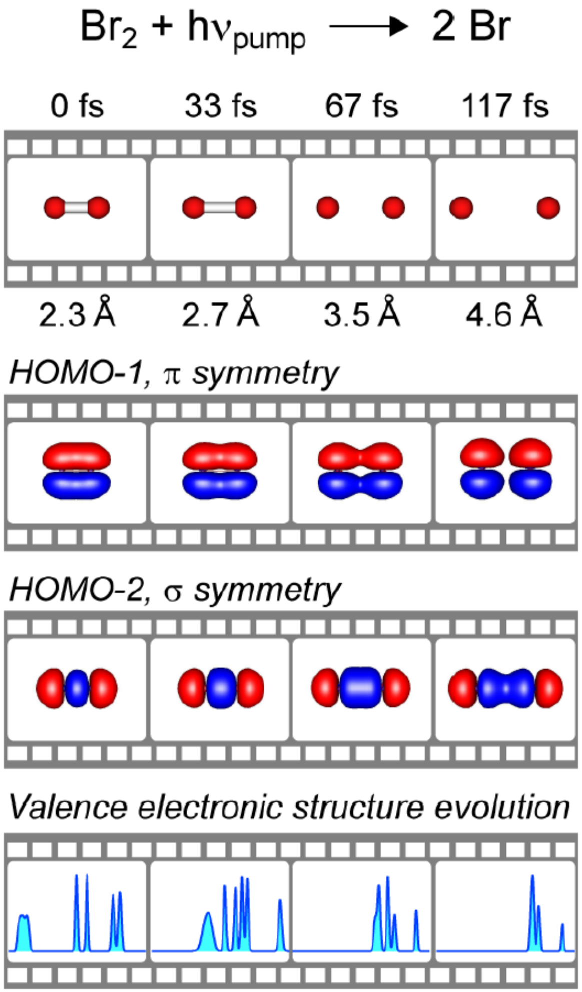
- $\Delta t \cdot \Delta E = \hbar$
- Time it takes to excite an atom = the scattering time Δt
- Associated with the transition of the atom from its initial to its final state
- Where ΔE is the energy transferred from to the atom
- May be given by $\Delta t = \hbar / \Delta E$
- For photo-excitation, specifically electronic excitation
- With an energy ΔE on the order of 5 eV transferred from the photon to the atom
- This corresponds to $\Delta t = 3 \cdot 10^{-17}$ s = 30 as (electronic excitation of 5 eV)

How fast do electrons move?

Take the Sommerfeld model of metals (Drude model + quantum theory)

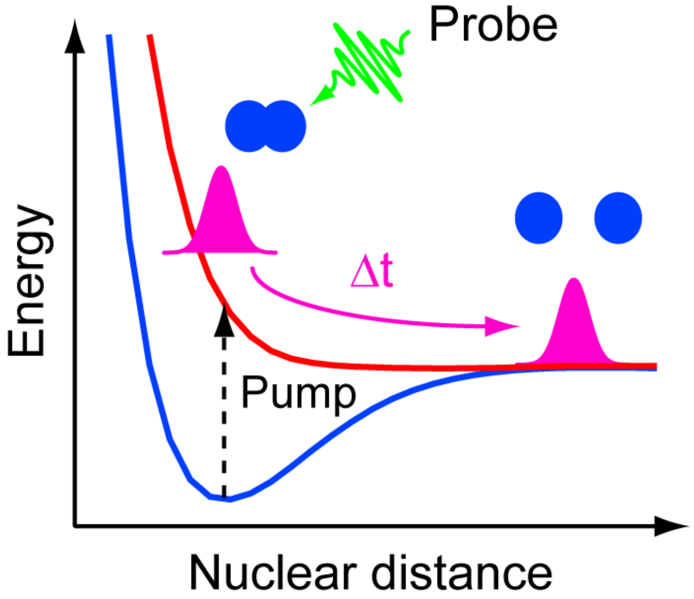
- For simplicity consider T = 0 K (doesn‘t limit the generality)
- Electrons are particles with momentum $p = \hbar k$ and velocity $v = \hbar k / m$
- Electrons are waves with wave vector k and de Broglie wavelength $\lambda = 2\pi/k$ (plane wave exp(i k r) e.g.)
- Fermi-Dirac distribution of velocities
- Occupied region in (quantized) k space containing all occupied one-electron levels is a sphere (Fermi sphere with Fermi surface) with radius k_F (largest possible wave vector)
- Fermi momentum h k_F = Momentum of the occupied one-electron levels of highest energy (Energy E_F)
- Fermi velocity $v_F = \hbar k_F/m$ = Velocity of the occupied one-electron levels of highest energy
- Fermi velocity is the velocity of Fermions (electrons) with kinetic energy = Fermi energy
- For most metals $v_F \approx 10^6$ m/s (e.g. Fe metal $2 \cdot 10^6$ m/s)
- Now it’s very simple: 10^6 m/s = $10^6\ 10^{10}$ Å/10^{-18} as = 1 Å/100 as (even at T = 0 K and 1% of speed of light…)

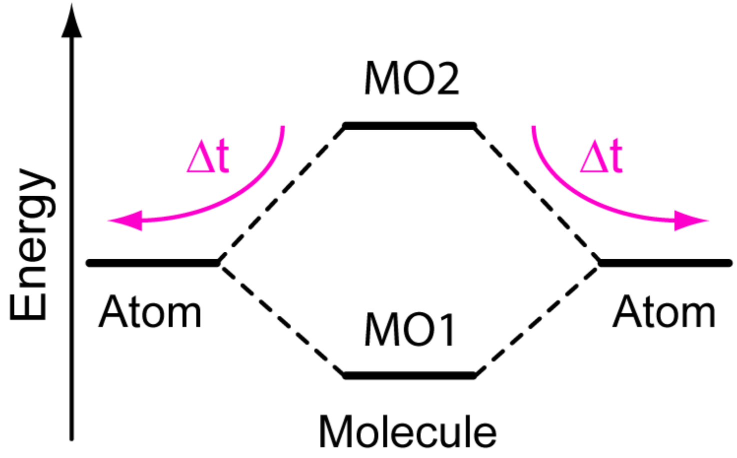
Electron rearrangements as nuclei are moving



Wernet et al., PRL **103**, 013001 (2009).

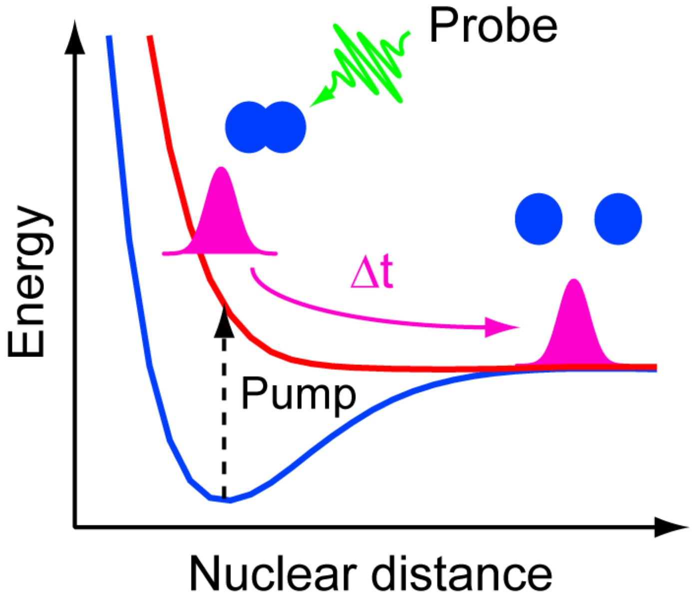
Mapping valence electron rearrangements

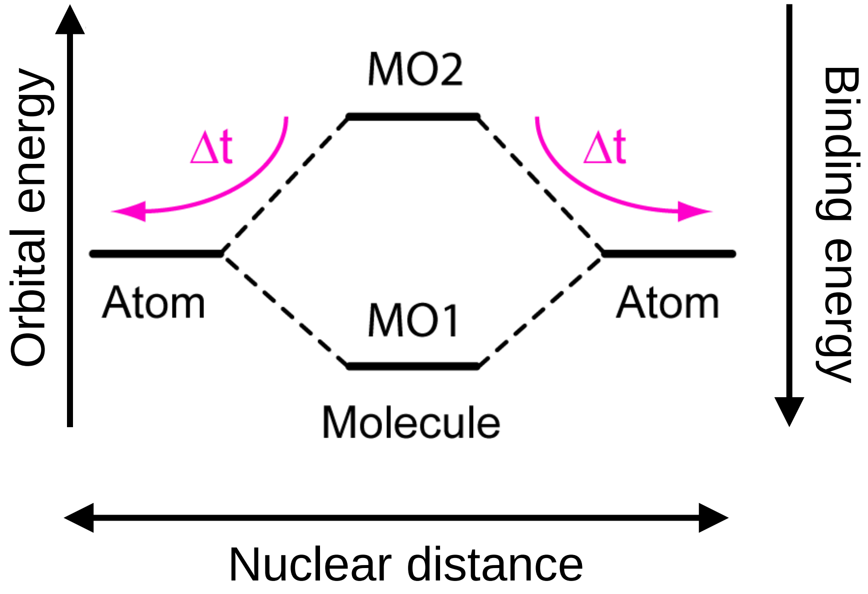




Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

Which one applies? Detect the differences…





Ashcroft Mermin *Solid State Physics*

Chap. 2, footnote 6

„State“ = State of N-electron system

„Level“ = One-electron state (e.g. orbital)

Koopmans' theorem: The first ionization energy of a molecular system is equal to the negative of the orbital energy of the highest occupied molecular orbital (HOMO).

Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

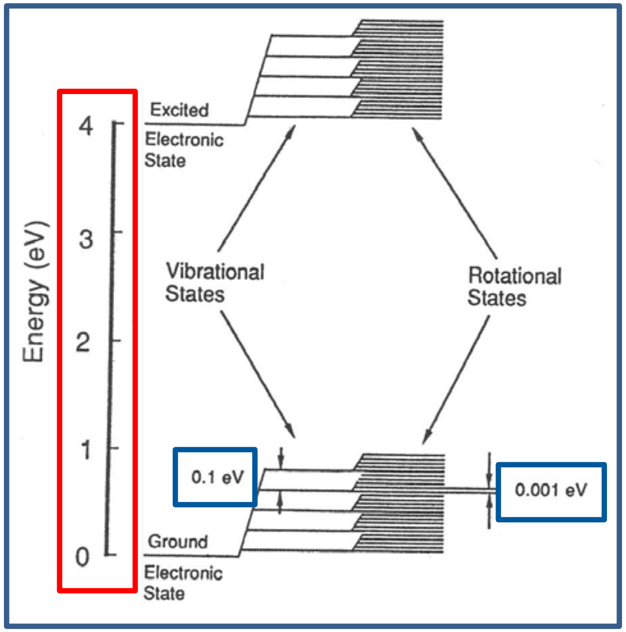
Discuss: What time-resolution do we need?

Say the temporal resolution corresponds to the pulse length

For Fourier-transform limited (Gaussian) pulses we have:

$$\Delta t_{FWHM} \cdot \Delta E_{FWHM} = 1.85 \text{ eV fs}$$

Svanberg
Atomic and Molecular Spectroscopy



20 fs, 0.1 eV

2 fs, 1 eV

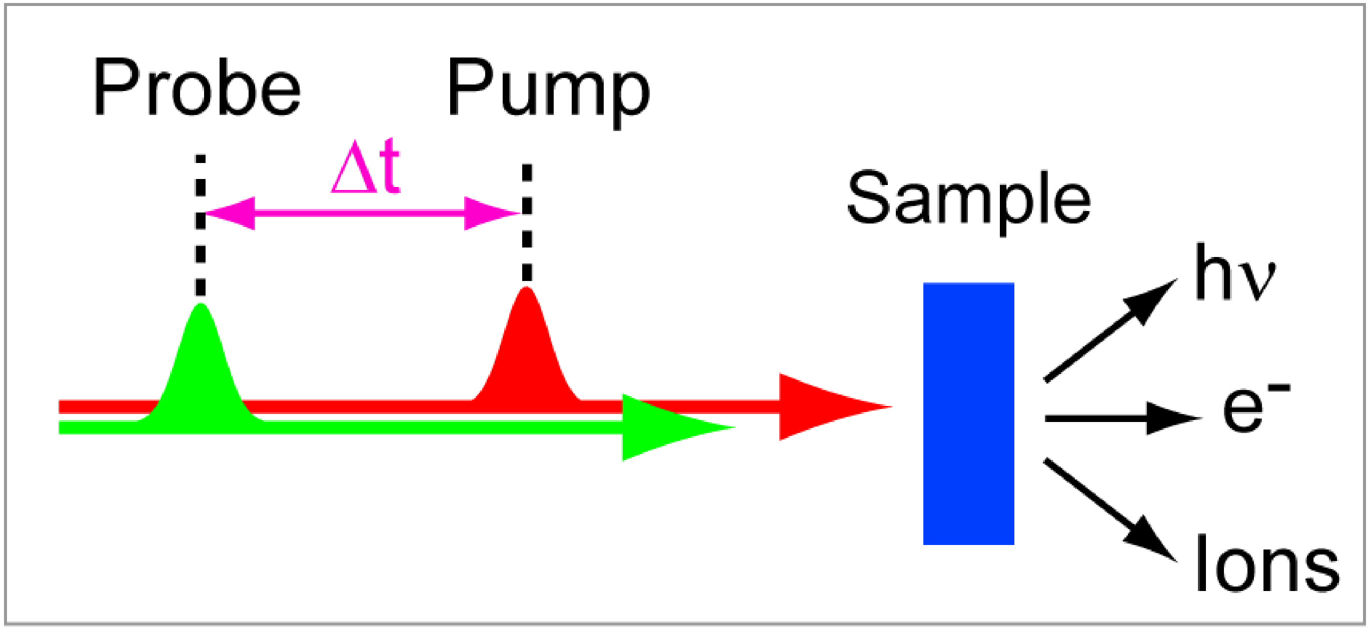
0.2 fs, 10 eV

Outline

1. “I think I need to tell you why…”
2. Setting the stage
3. Some basics
4. **Methods**
5. One application
6. One of many possible outlooks

Pump-probe spectroscopy

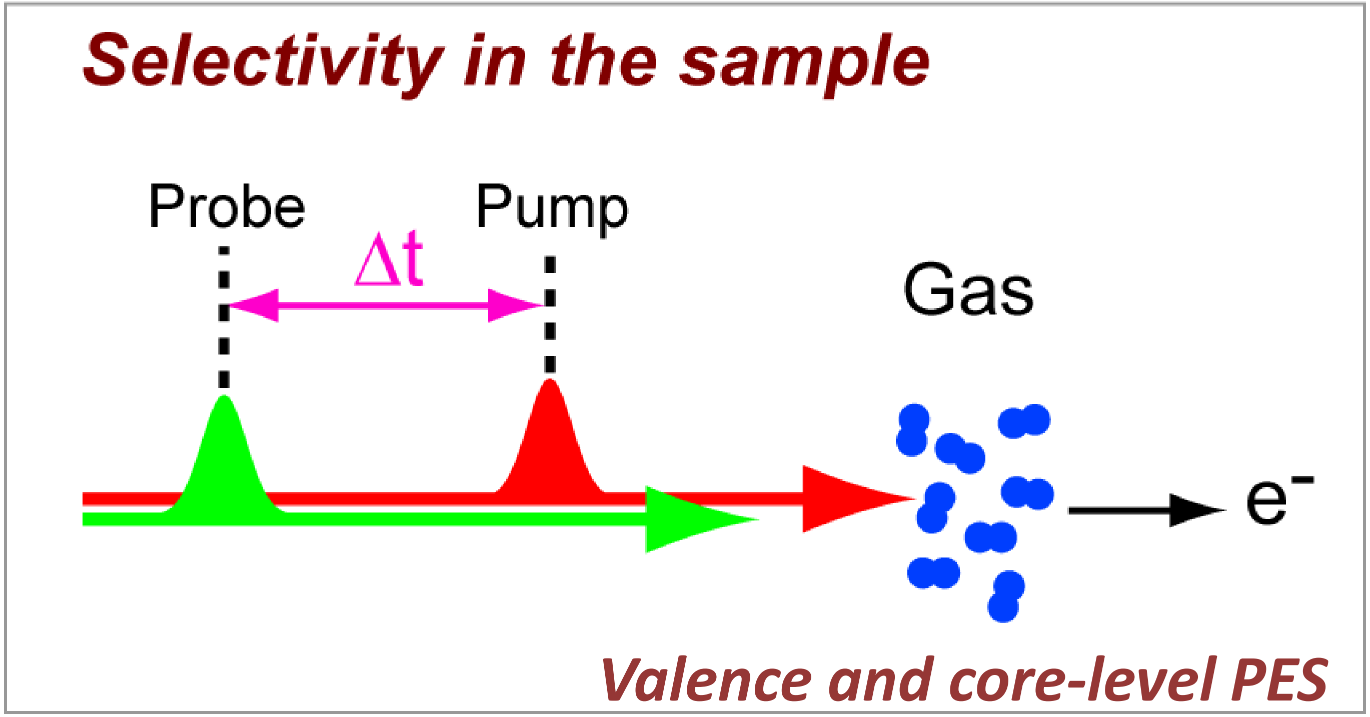
Optical pump and x-ray probe



Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

Pump-probe spectroscopy

Optical pump and x-ray probe

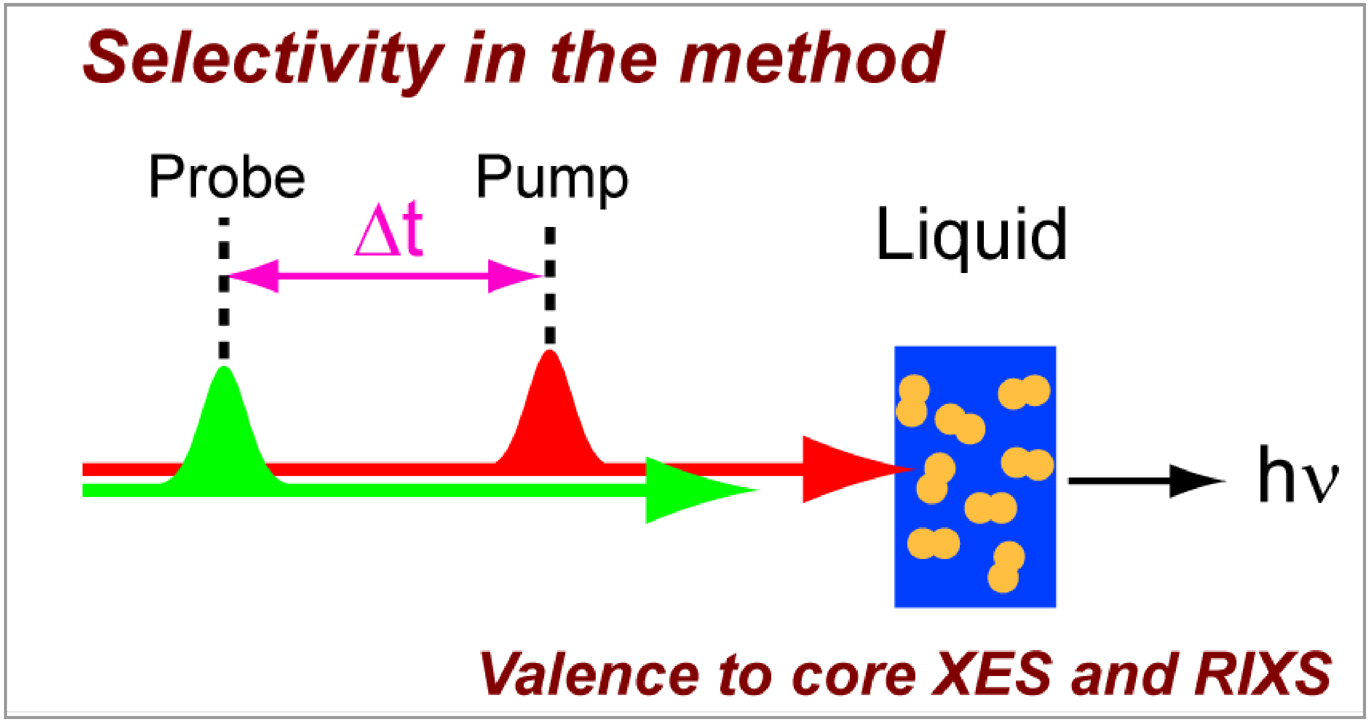


Valence and core-level PES

Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

Pump-probe spectroscopy

Optical pump and x-ray probe



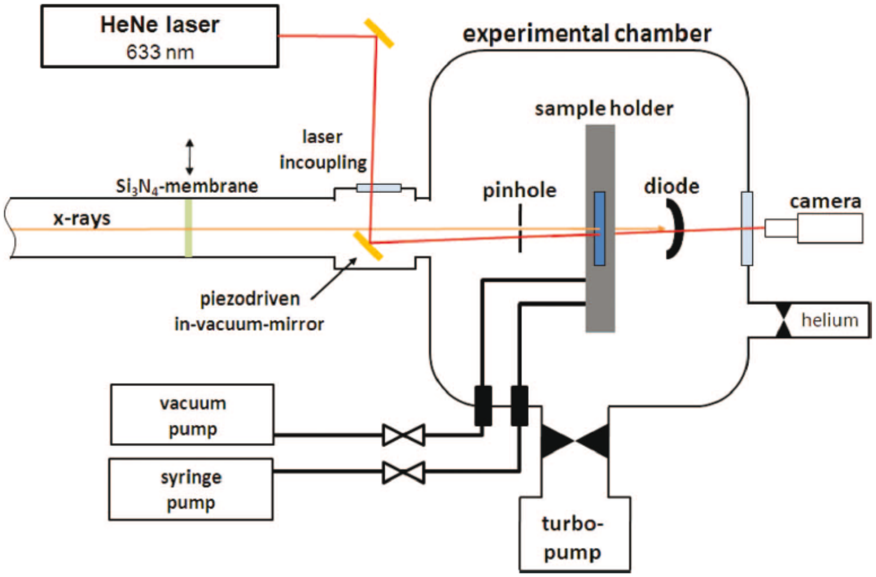
Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

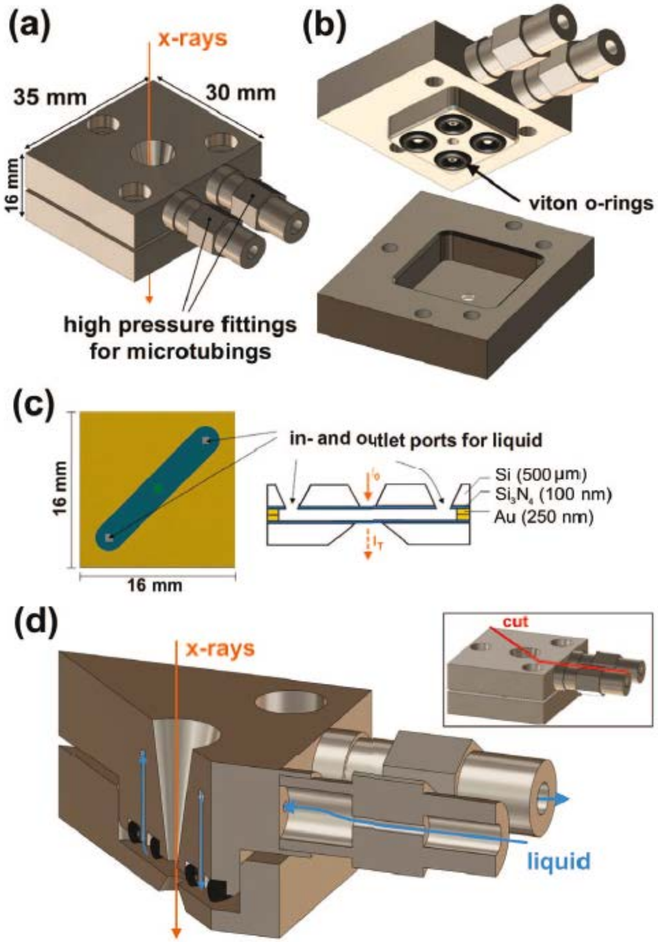
Preparation of liquid samples

For soft x-ray spectroscopy (UH-vacuum!)

- Cells for transmission + fluorescence
- Jets for fluorescence
- Flat jets for transmission

Cells for transmission



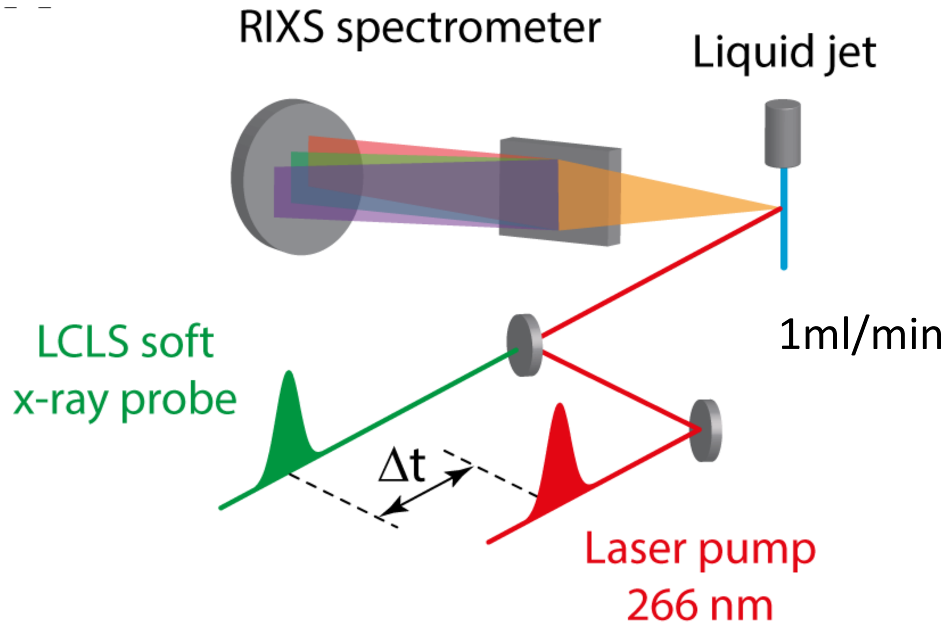


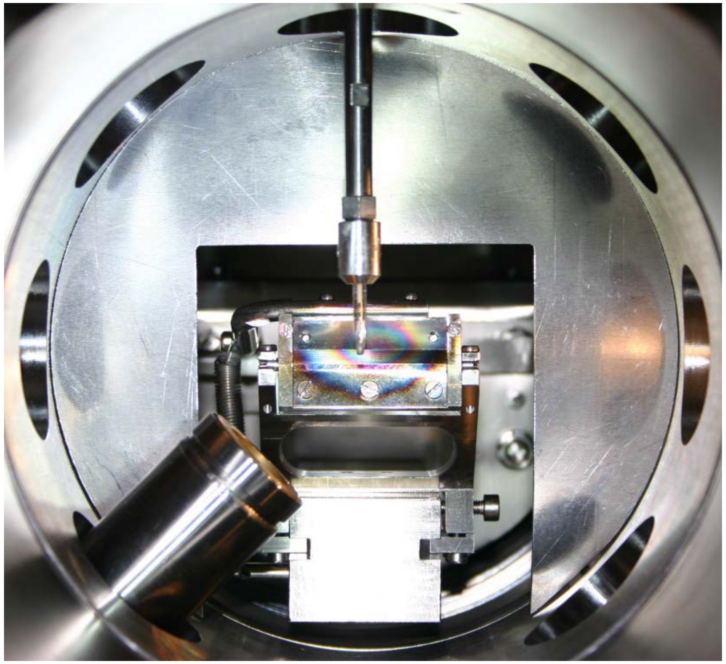
Schreck, Gavrila, Weniger, Wernet, Rev. Sci. Instrum. **82**, 103101 (2011)

Meibohm, Schreck, Wernet, Rev. Sci. Instrum. **85**, 103102 (2014)

Similar realizations by Nils Huse and Nobuhiro Kosugi!

Jets for fluorescence

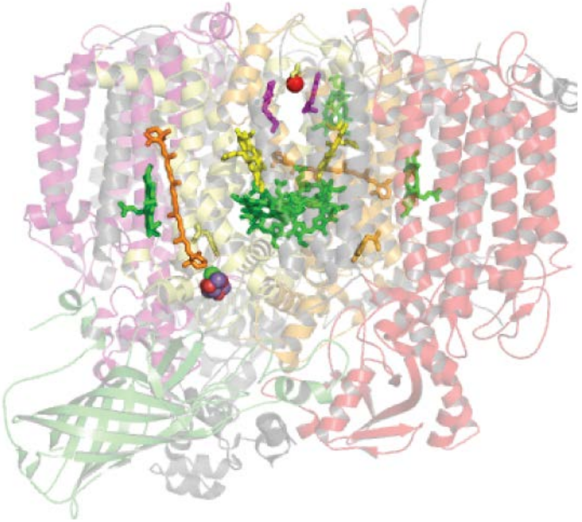


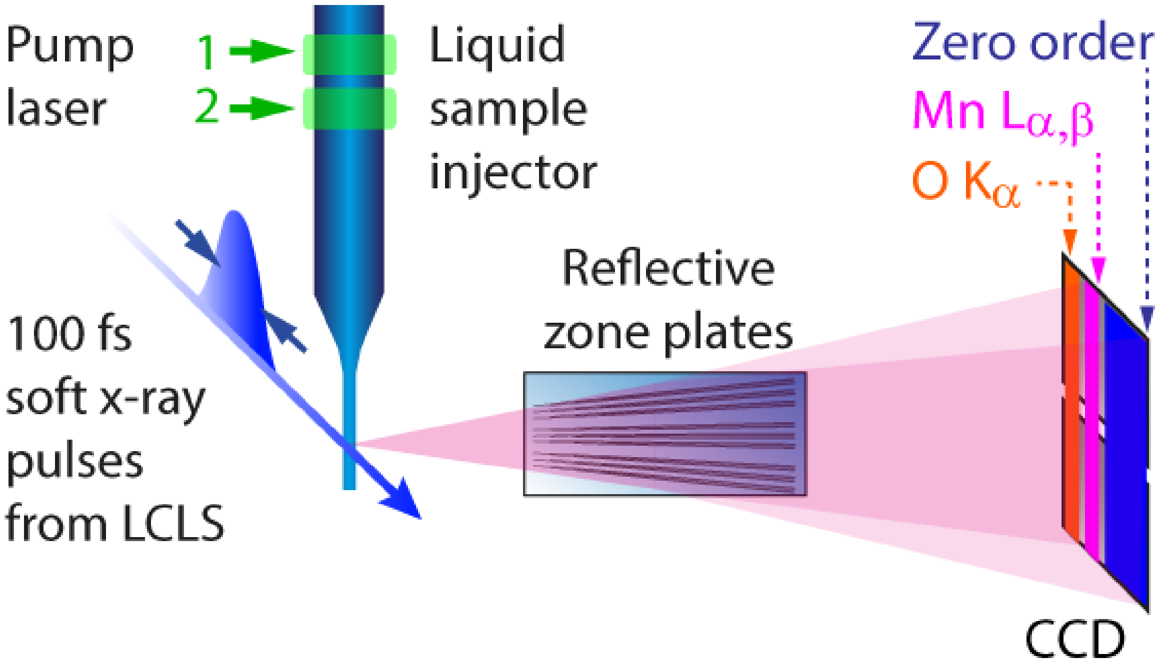


K. Kunnus et al. Rev. Sci. Instrum. **83**, 123109 (2012).
Ph. Wernet et al. Nature **520**, 78-81 (2015).

Jets for fluorescence

Photosystem II





Pump laser

1

2

Liquid sample injector

100 fs soft x-ray pulses from LCLS

Reflective zone plates

Zero order

Mn Lα,β

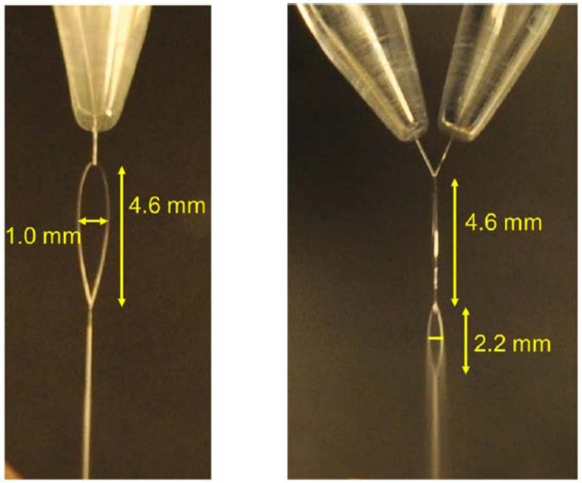
O Kα

CCD

Kubin, Kern, …, Borovik, Agapie, Messinger, …, Bergmann, Mitzner, Yachandra, Yano, Wernet, Structural Dynamics **4**, 054307 (2017).

Flat jets for transmission

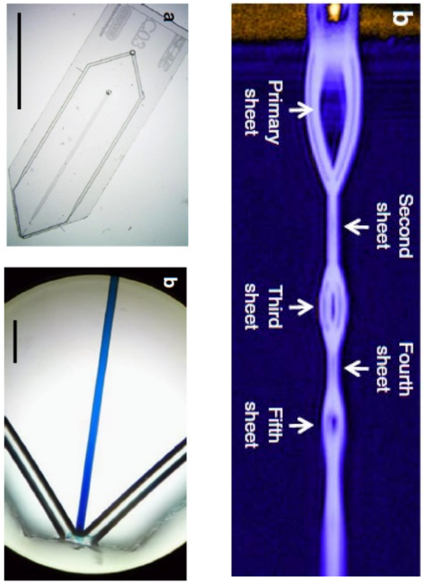
Colliding jets



Ekimova, Quevedo, Faubel, Wernet, Nibbering, Struct. Dyn. **2**, 054301 (2015)

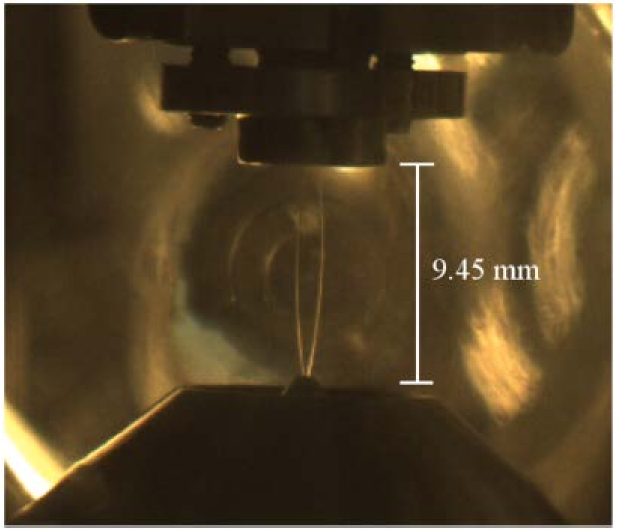
Fondell et al., Struct. Dyn. **4**, 054902 (2017)

Microfluidic gas-dynamic nozzle



Koralek et al., Nat. Commun. **9**, 1353 (2018)

Rectangular nozzle



Galinis et al., Rev. Sci. Instrum. **88**, 083117 (2017)

Outline

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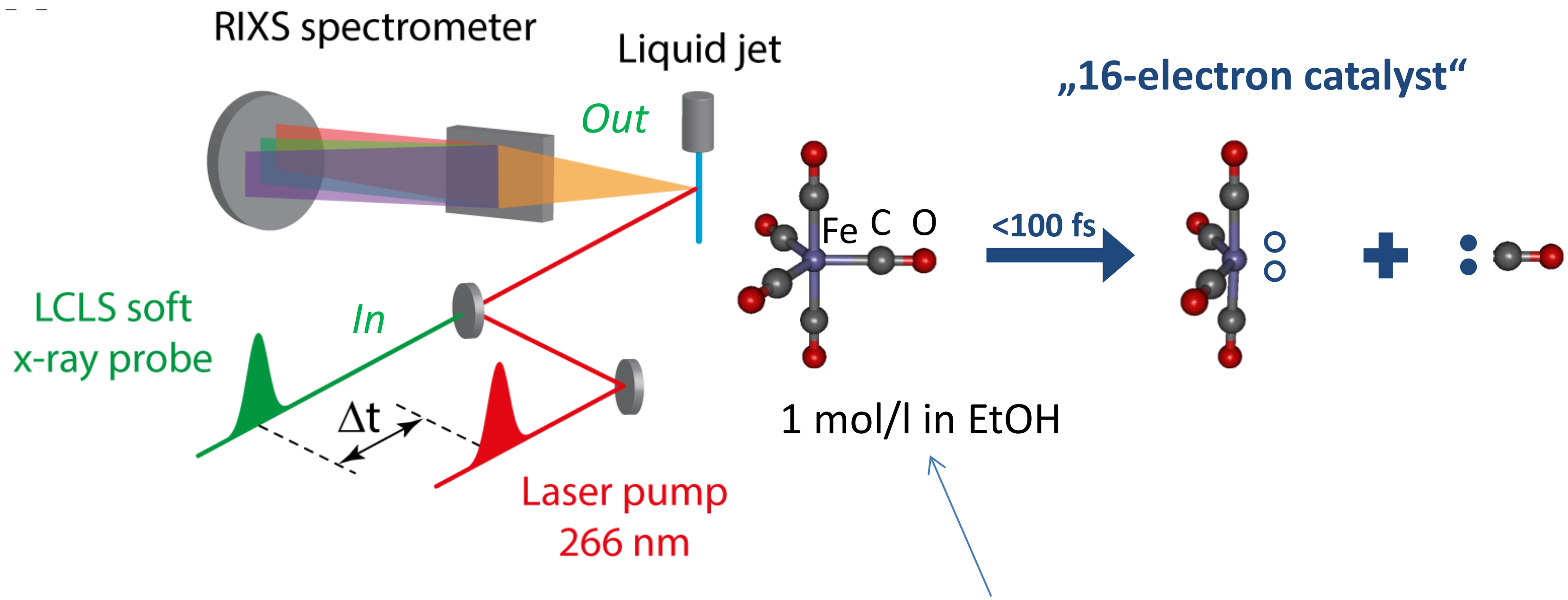
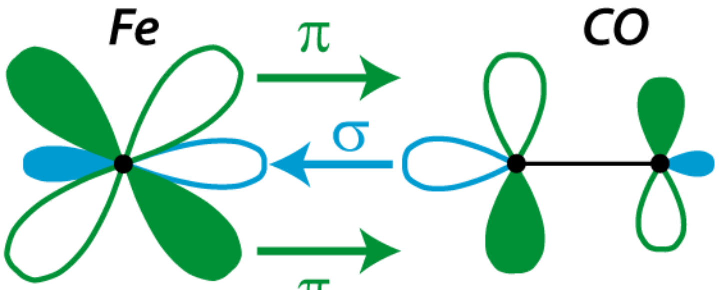
Time-resolved RIXS at LCLS



K. Kunnus et al. Rev. Sci. Instrum. **83**, 123109 (2012).
Ph. Wernet et al. Nature **520**, 78-81 (2015).

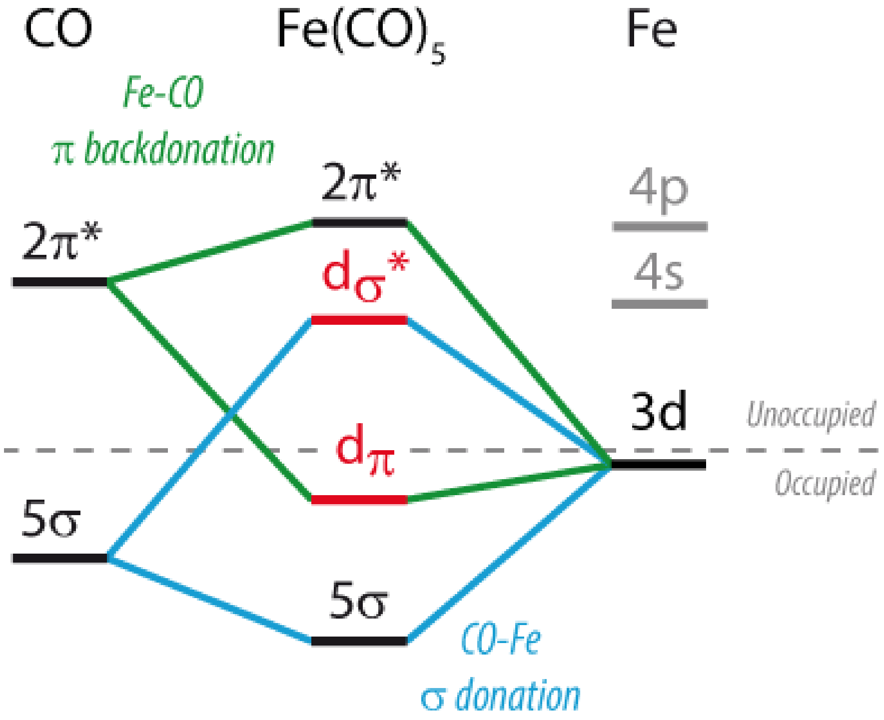
Bonding in $Fe(CO)_5$

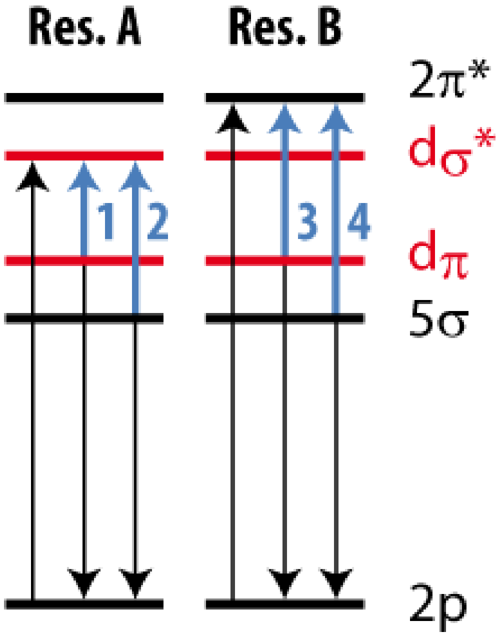
Ligand to metal sigma donation



Metal to ligand pi back-donation

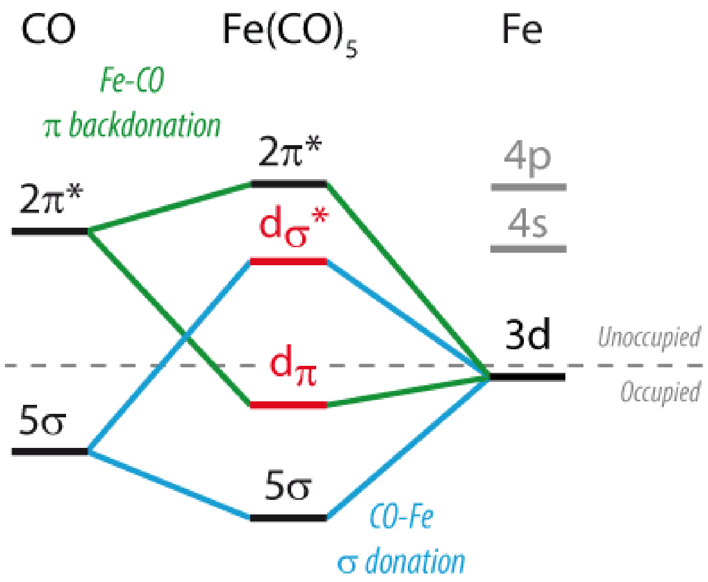
RIXS of $Fe(CO)_5$

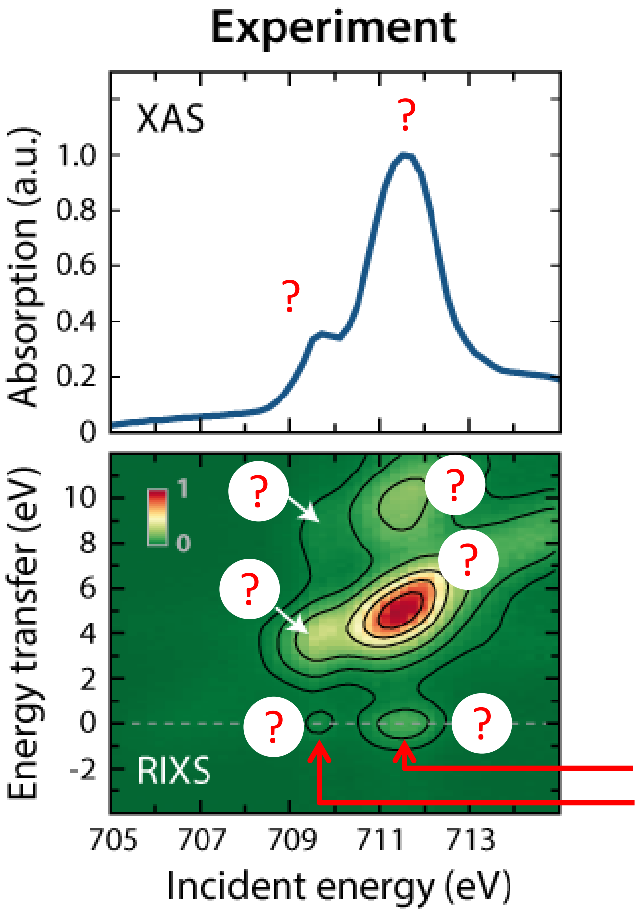


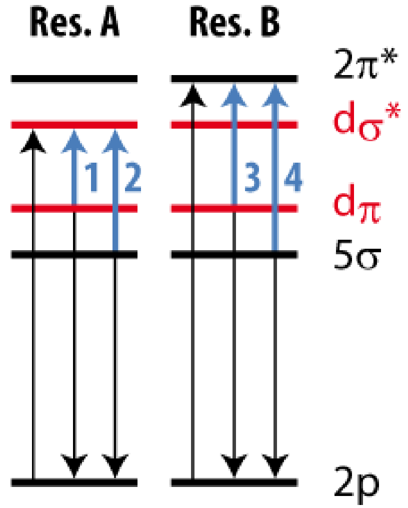


Book chapter in „X-Ray Free Electron Lasers“ by J. Yano, V. Yachandra, U. Bergmann (Eds.), *Royal Society of Chemistry Energy and Environment Series*, Ph. Wernet (2016).

You do the job: Assign the features!







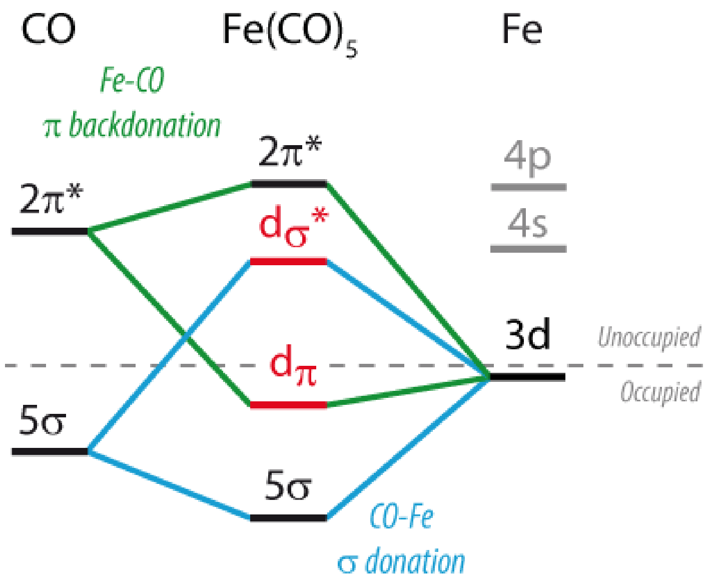
2p→2π*→2p

2p→dσ*→2p

Resonant scattering!

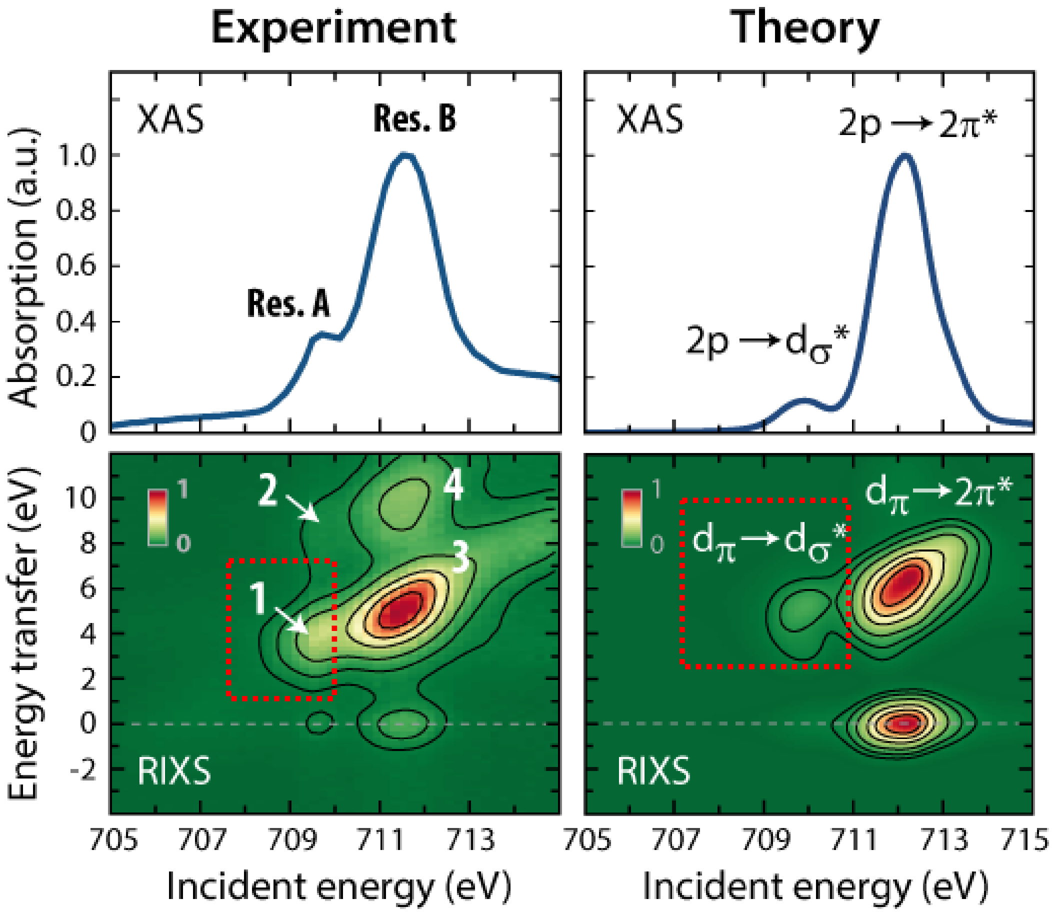
Book chapter in „X-Ray Free Electron Lasers“ by J. Yano, V. Yachandra, U. Bergmann (Eds.), *Royal Society of Chemistry Energy and Environment Series*, Ph. Wernet (2017).

RIXS of $Fe(CO)_5$

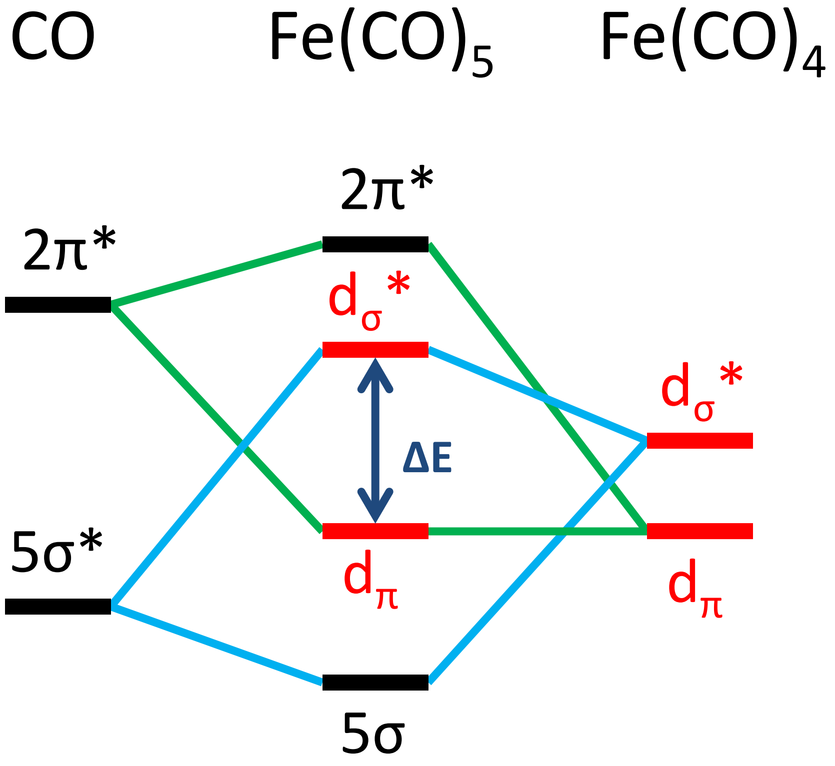


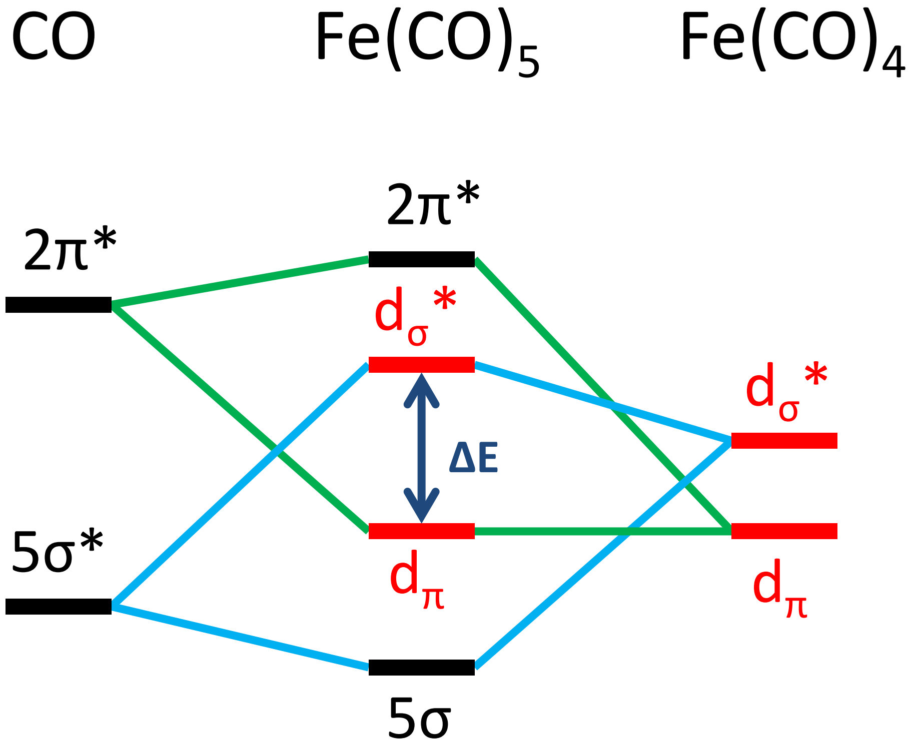
Let‘s focus on these transitions because they involve the frontier orbitals HOMO and LUMO!

5σ not included (transitions 2 and 4 missing)!



Book chapter in „X-Ray Free Electron Lasers“ by J. Yano, V. Yachandra, U. Bergmann (Eds.), *Royal Society of Chemistry Energy and Environment Series*, Ph. Wernet (2017).


CO
$Fe(CO)_5$
$Fe(CO)_4$
$2\pi^*$
$2\pi^*$
d_σ^*
d_σ^*
ΔE
$5\sigma^*$
d_π
d_π
5σ



CO

$Fe(CO)_5$

$Fe(CO)_4$

$2\pi^*$

$5\sigma^*$

$2\pi^*$

d_σ^*

ΔE

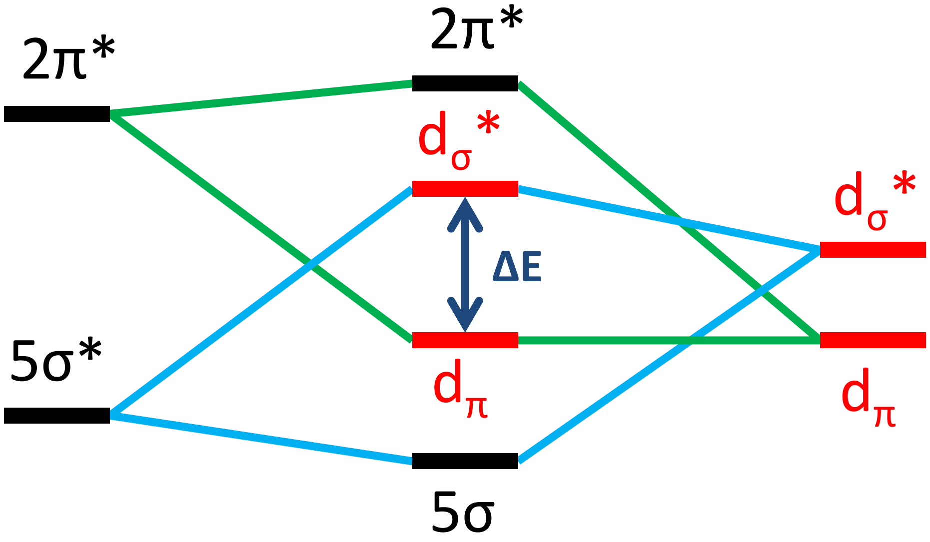
d_π

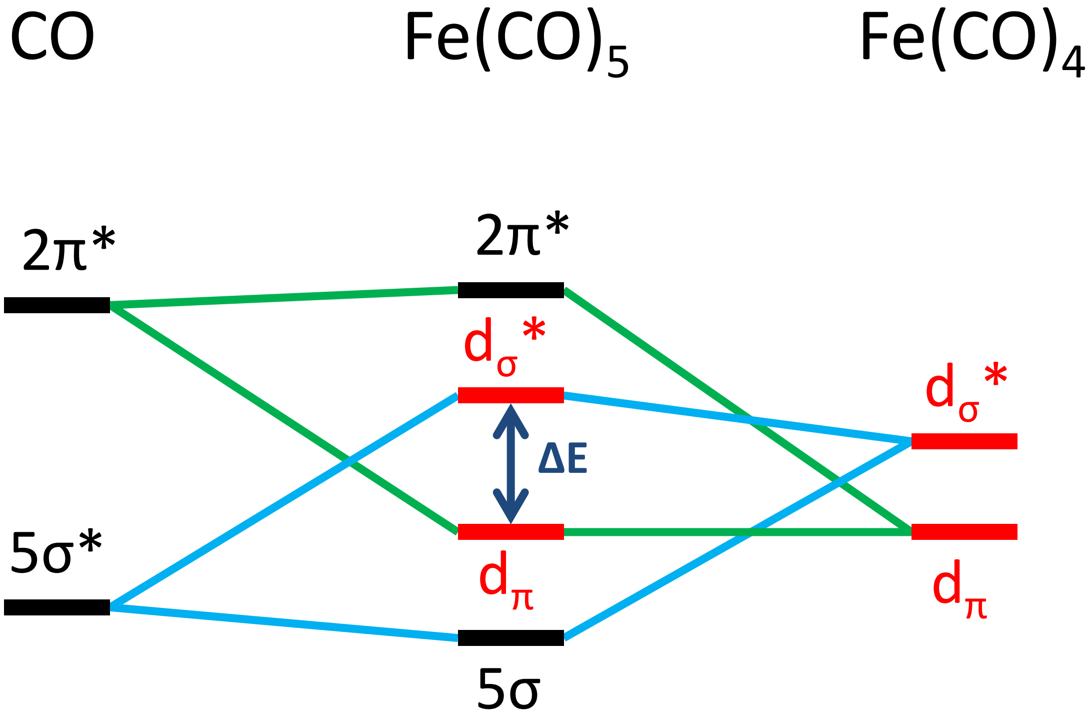
5σ

d_σ^*

d_π

CO $\quad$ $Fe(CO)_5$ $\quad$ $Fe(CO)_4$





CO

$Fe(CO)_5$

$Fe(CO)_4$

$2\pi^*$

$2\pi^*$

$d_\sigma{}^*$

$d_\sigma{}^*$

ΔE

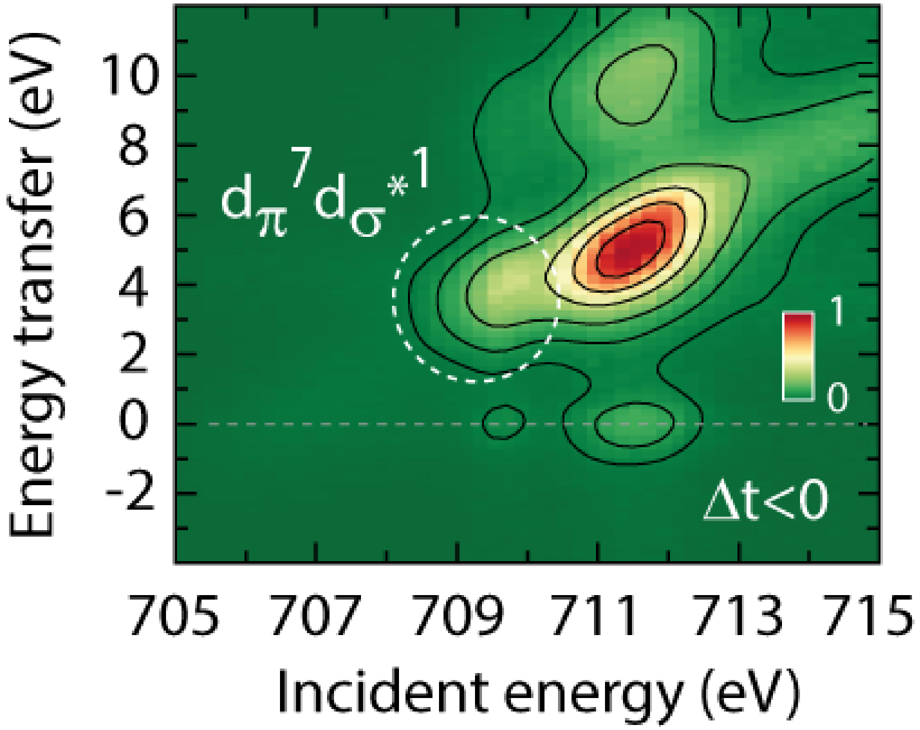
$5\sigma^*$

d_π

d_π

5σ

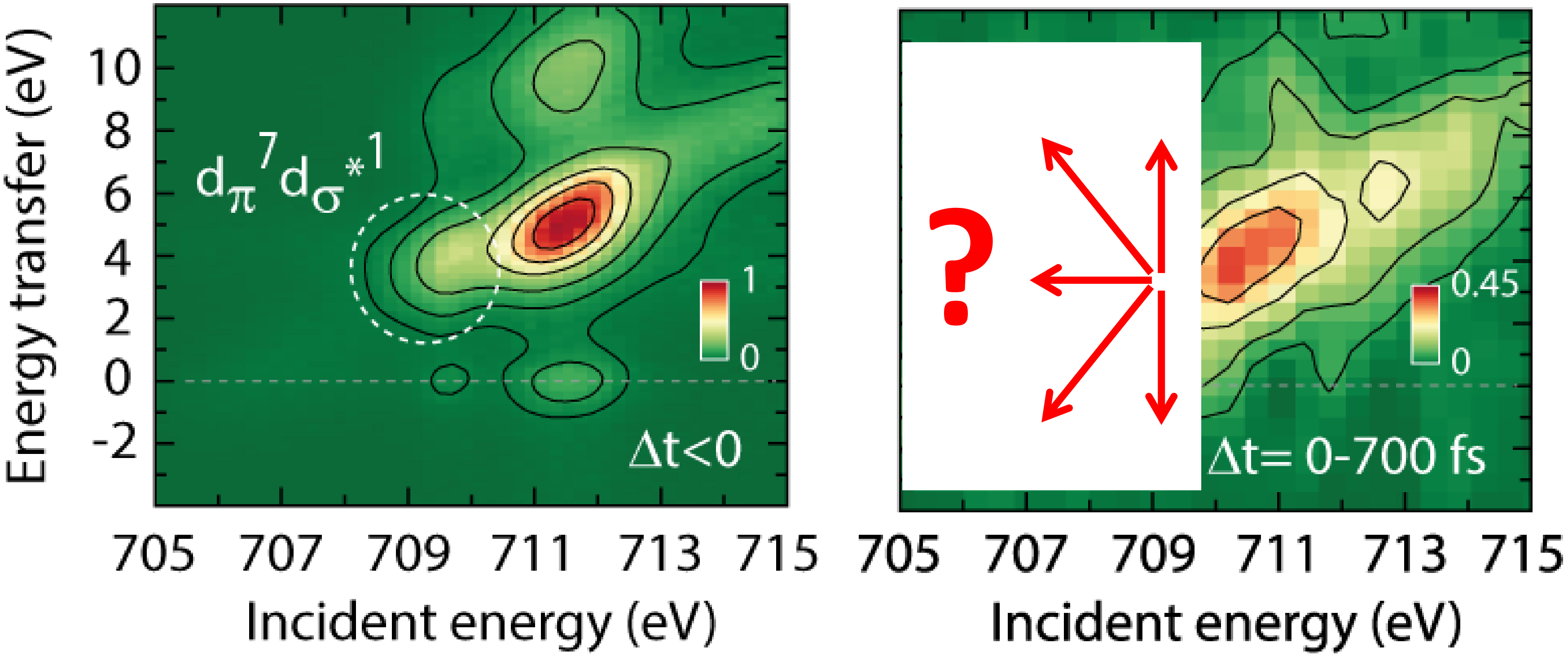
$Fe(CO)_5$



Fe L_3-absoprtion edge

Predict the experimental outcome!

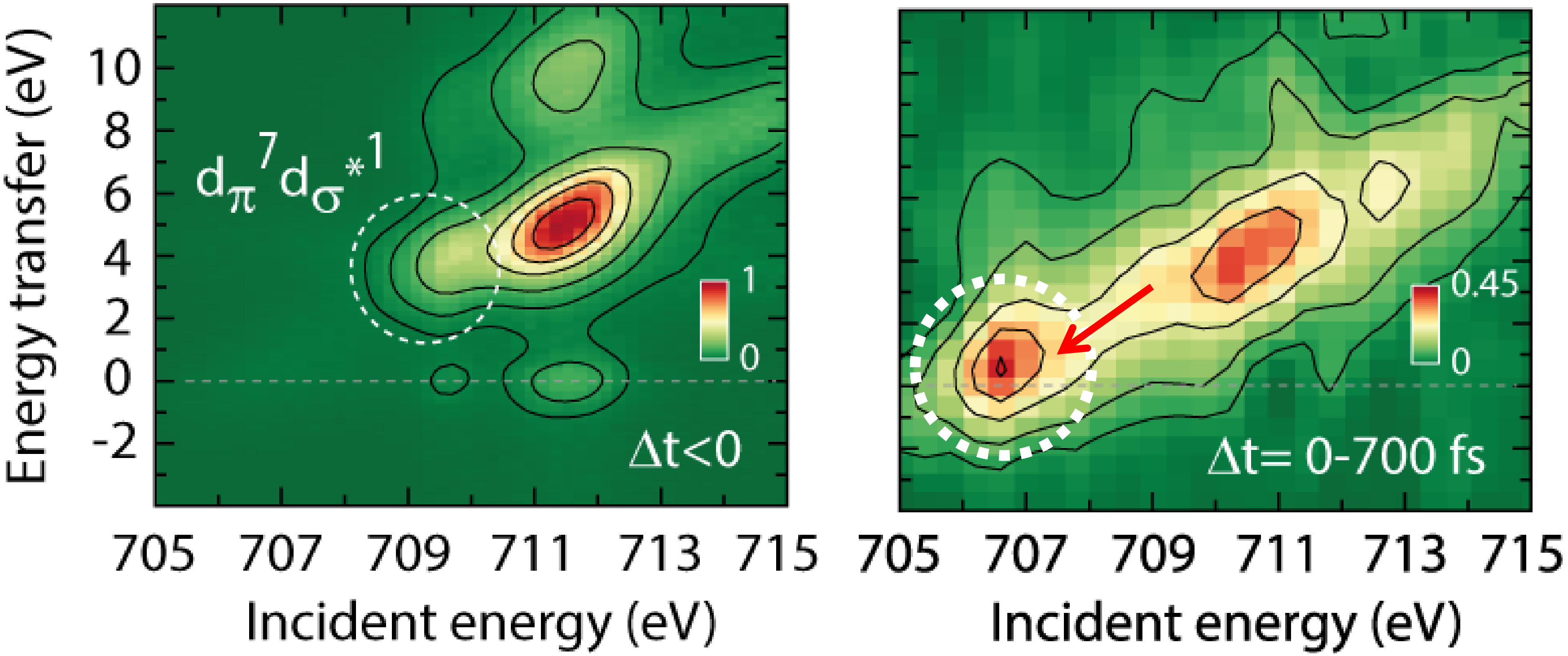
$Fe(CO)_5$ **$Fe(CO)_4$ fragments**



Fe L_3-absoprtion edge

$Fe(CO)_5$

$Fe(CO)_4$ fragments

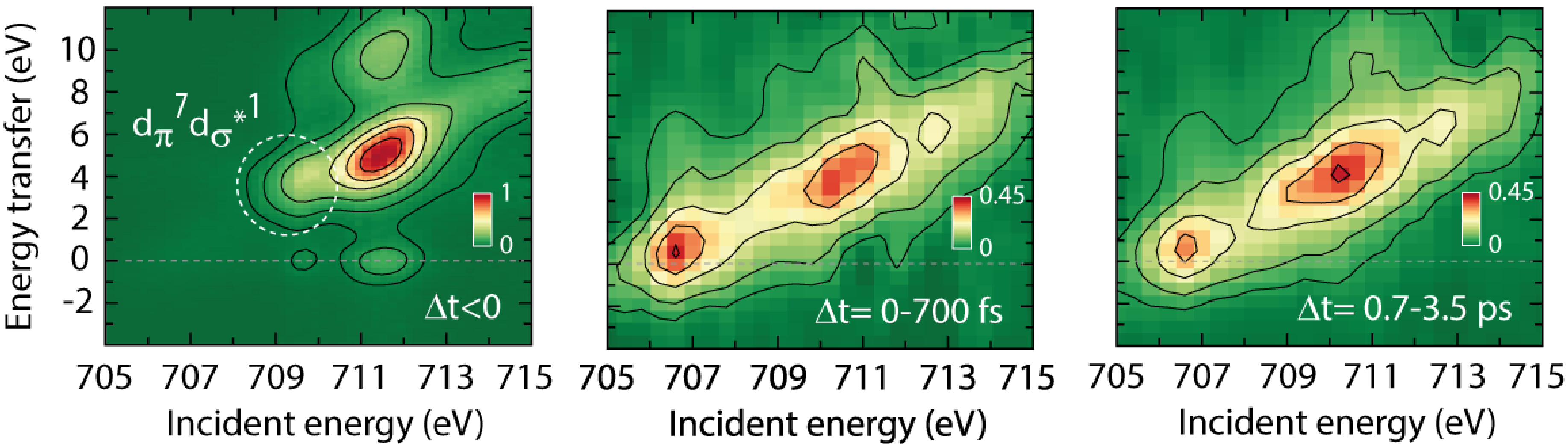


Delays between 0 and 700 fs mashed together for the moment!

Ph. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, W. Quevedo, M. Beye, S. Schreck, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. de Groot, K. J. Gaffney, S. Techert, M. Odelius, A. Föhlisch, Nature **520**, 78-81 (2015).

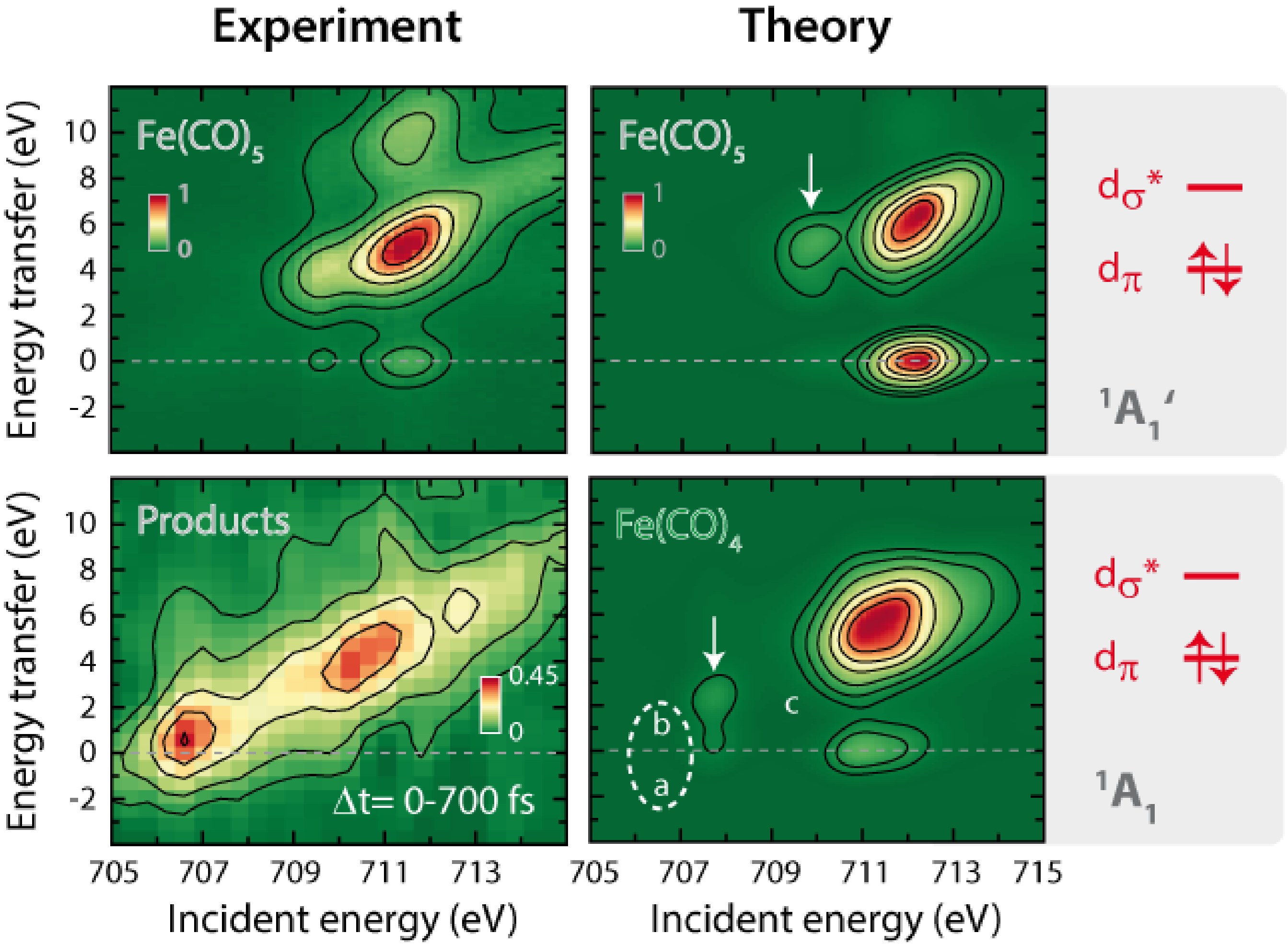
$Fe(CO)_5$ $Fe(CO)_4$ fragments

Early *Late*



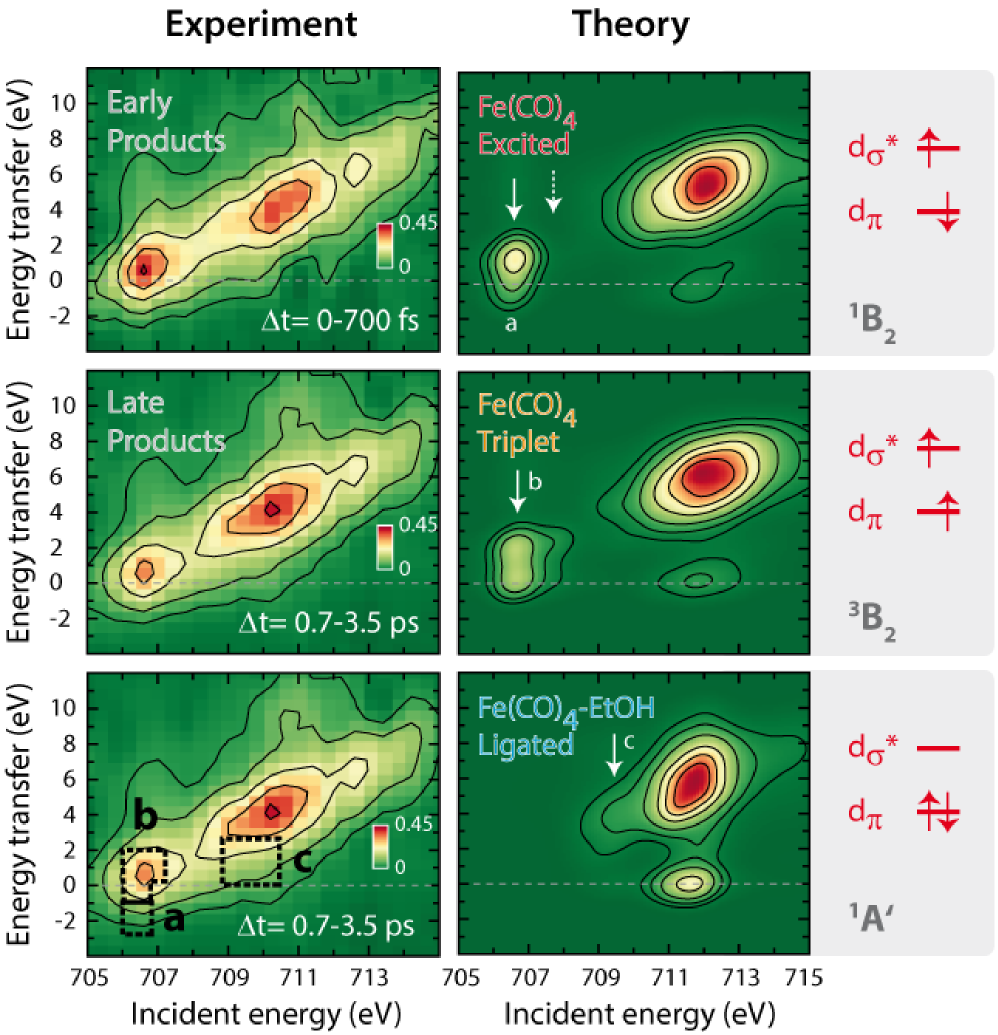
Ph. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, W. Quevedo, M. Beye, S. Schreck, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. de Groot, K. J. Gaffney, S. Techert, M. Odelius, A. Föhlisch, Nature **520**, 78-81 (2015).

Characterize species with calculations



Book chapter in „X-Ray Free Electron Lasers“ by J. Yano, V. Yachandra, U. Bergmann (Eds.), *Royal Society of Chemistry Energy and Environment Series*, Ph. Wernet (2017).

Characterize species with calculations



RIXS from an excited state (Anti-Stokes)

RIXS from a triplet species (intersystem crossing)

RIXS from ligated species (solvent ligation)

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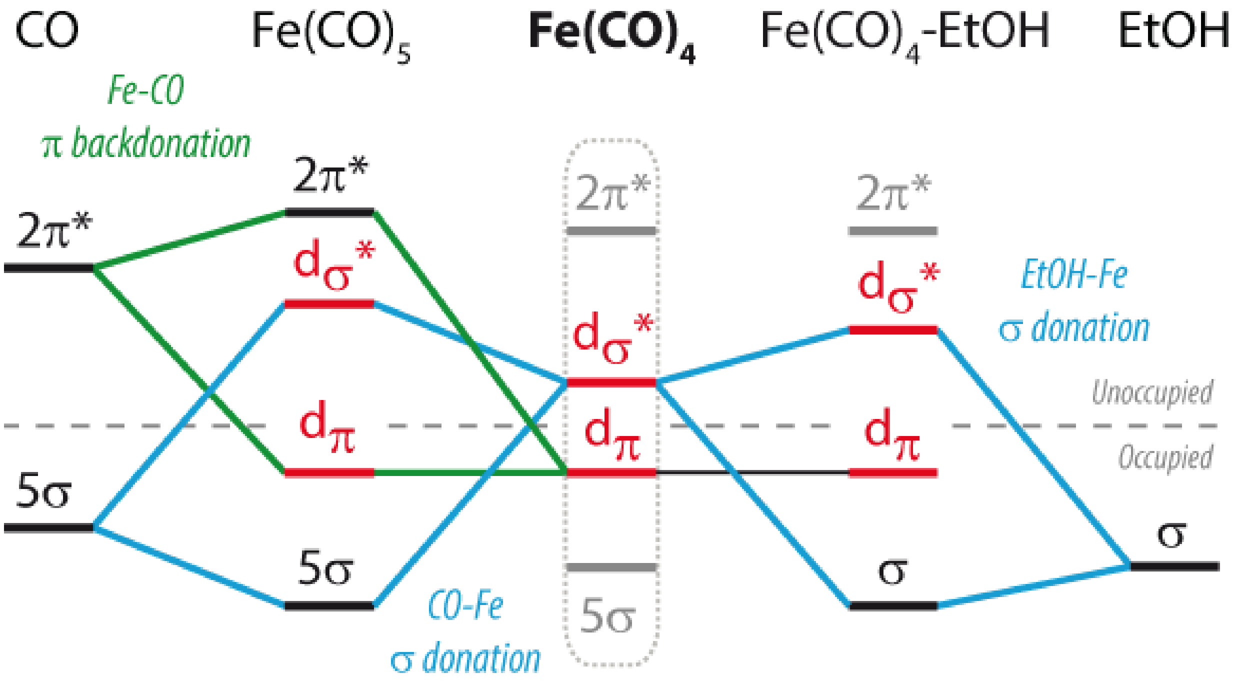
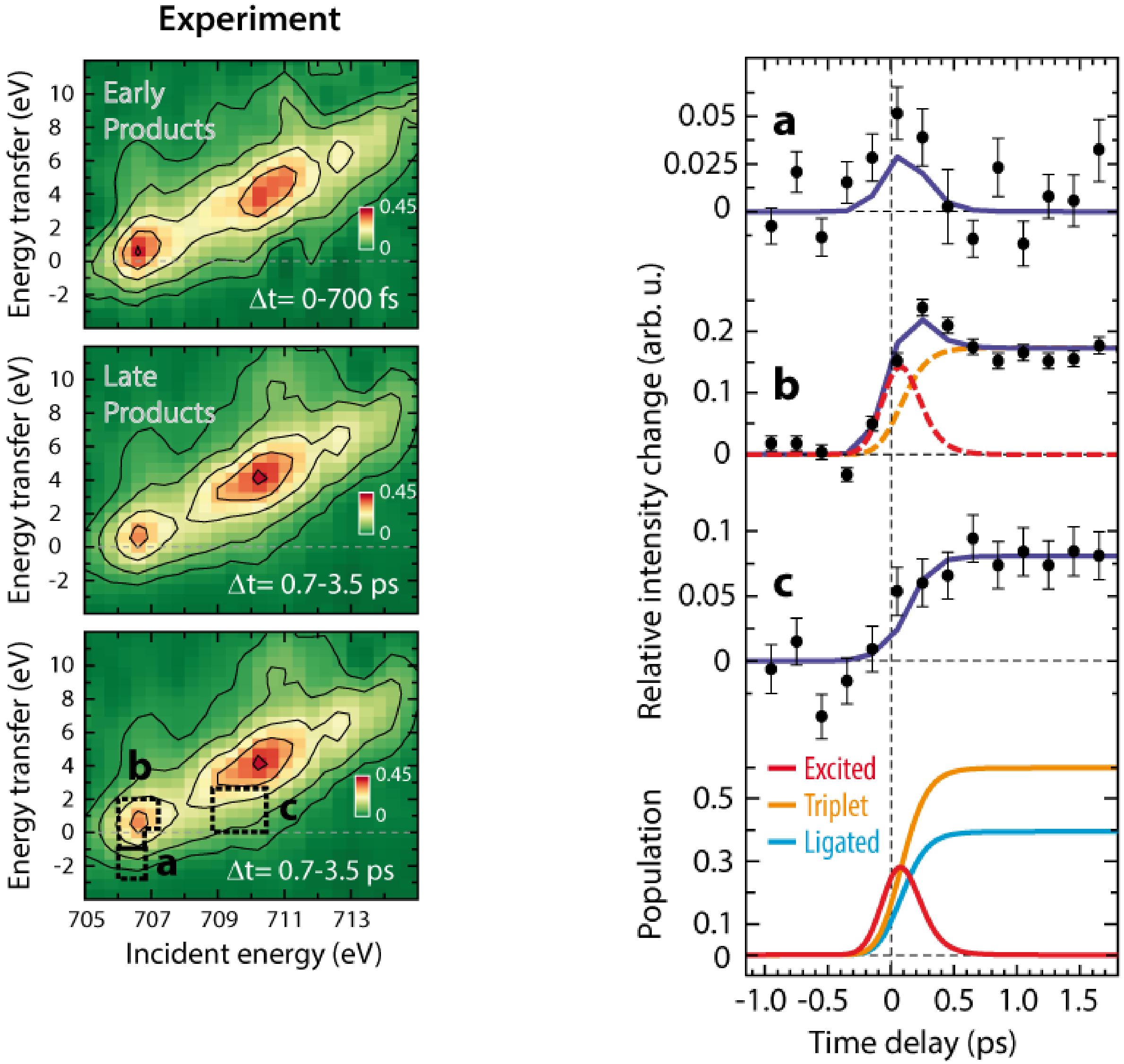
Solvent ligation

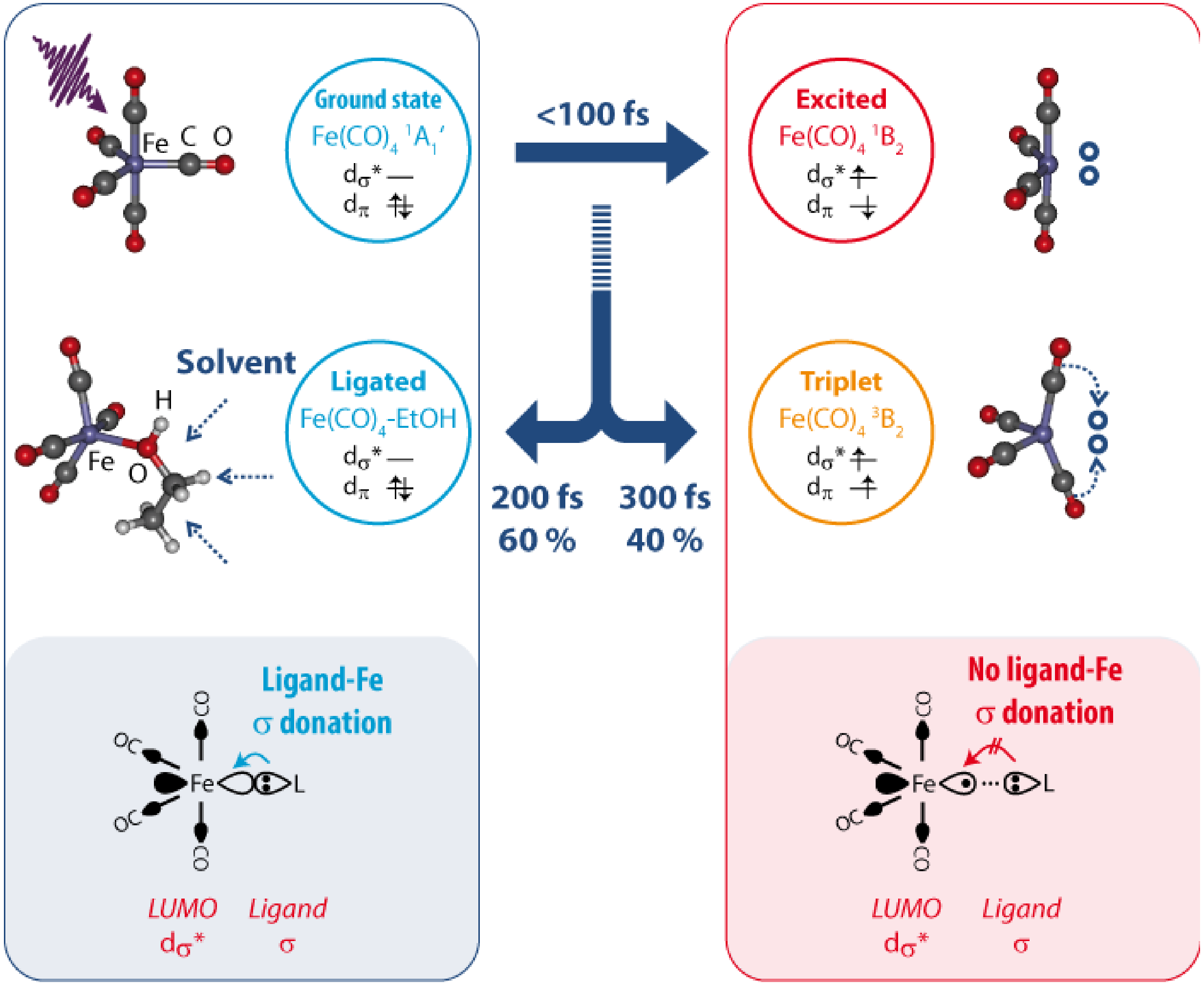


Book chapter in „X-Ray Free Electron Lasers“ by J. Yano, V. Yachandra, U. Bergmann (Eds.), *Royal Society of Chemistry Energy and Environment Series*, Ph. Wernet (2017).

Temporal evolution

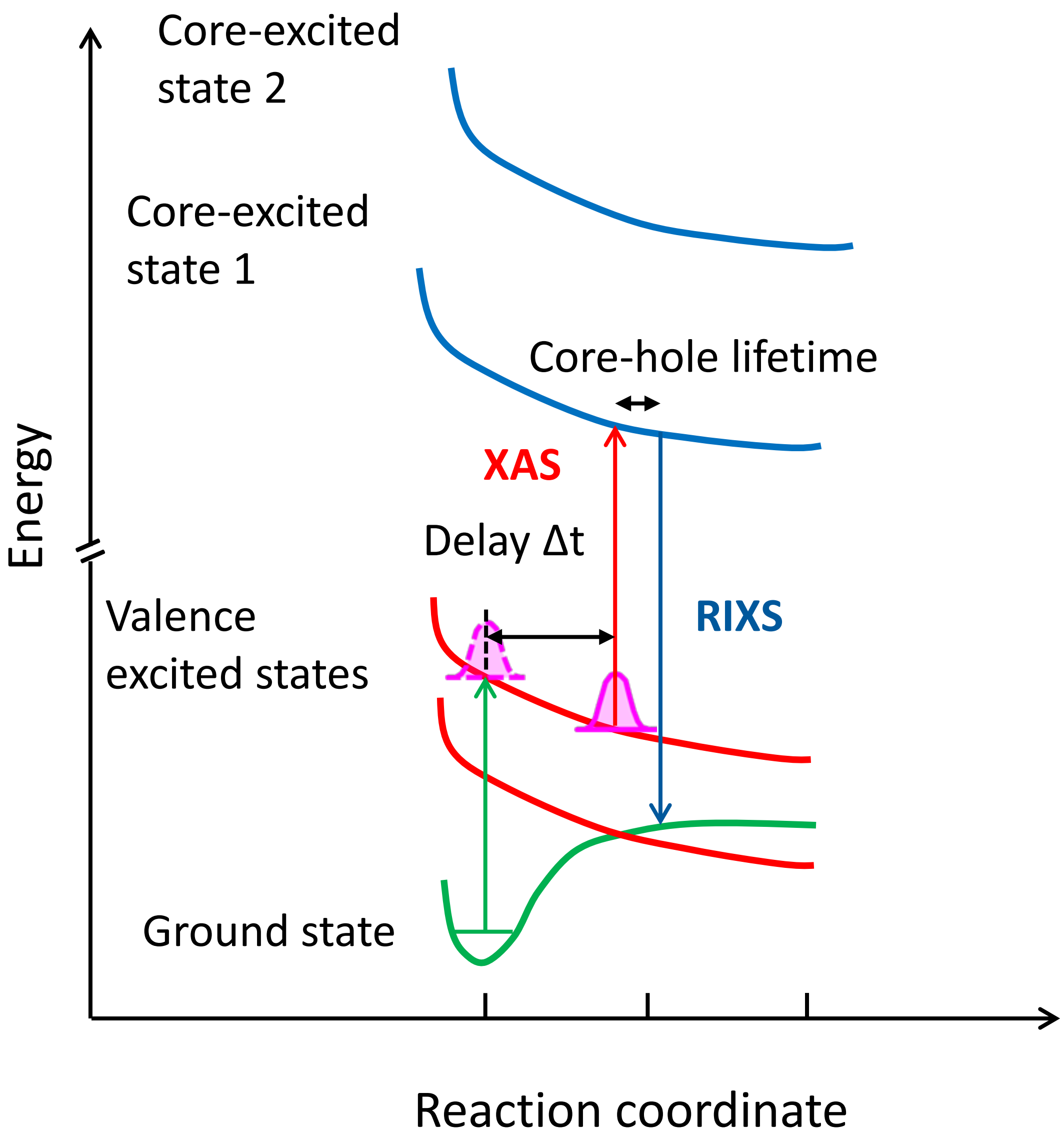


Simple, conceptual conclusions



Book chapter in „X-Ray Free Electron Lasers“ by J. Yano, V. Yachandra, U. Bergmann (Eds.), *Royal Society of Chemistry Energy and Environment Series*, Ph. Wernet (2016).

Where are the arrows for XAS and RIXS?



Outline

1. “I think I need to tell you why…”
2. Setting the stage
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6. **One of many possible outlooks**

Current XFELs

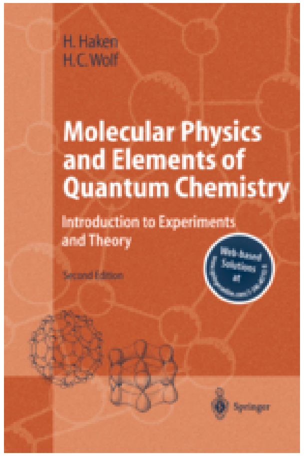
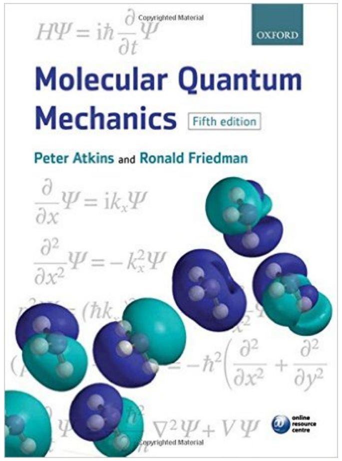
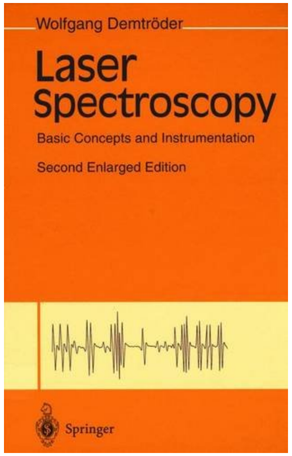
100 Hz
Concentrations 1 mol/l

→

LCLS-II, EU-XFEL,…

100 kHz
Concentrations 1-10 mmol/l

Further reading

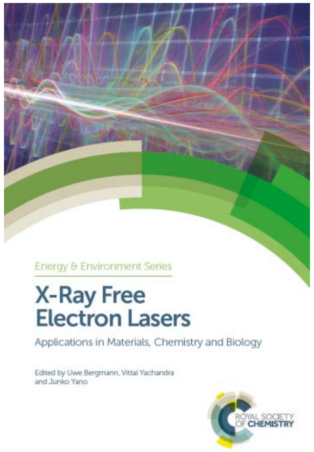





Haken/Wolf *Molecular Physics and Elements of Quantum Chemistry*

Atkins/Friedman *Molecular Quantum Mechanics*

Demtröder *Laser Spectroscopy*

Ashcroft Mermin *Solid State Physics*



X-Ray Free Electron Lasers – Applications in Materials, Chemistry and Biology
Royal Society of Chemistry Energy and Environment Series)
J. Yano, V. Yachandra, U. Bergmann (Eds.) (2016).

EXTRA SLIDES

Outline

1. “I think I need to tell you why…”
2. **Setting the stage**
3. Some basics
4. Methods
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6. One of many possible outlooks

Chemical and thermodynamic equilibrium 1

Chemical equilibrium:

$Reactants \rightleftarrows Products$ e.g.: $A + B \rightleftarrows C + D$

$$Rate = \frac{d[Products]}{dt} \;\alpha\; [Reactants]$$

α: Proportional to

[…]: Concentration of …

e.g. $Rate = \frac{d[C]}{dt} \alpha\, [A] \cdot [B]$ (neglecting stochiometry and reaction order)

Proportionality constant k (rate konstant):

$$Rate = k \;\cdot [Reactants]$$

The rate (the rate konkstant) quantifies the speed/the efficiency of the reaction.

Chemical and thermodynamic equilibrium 2

$$Rate\ forward = Rate\ backward$$

$$k_{forward} \cdot [Reactants] = k_{backward} \cdot [Products]$$

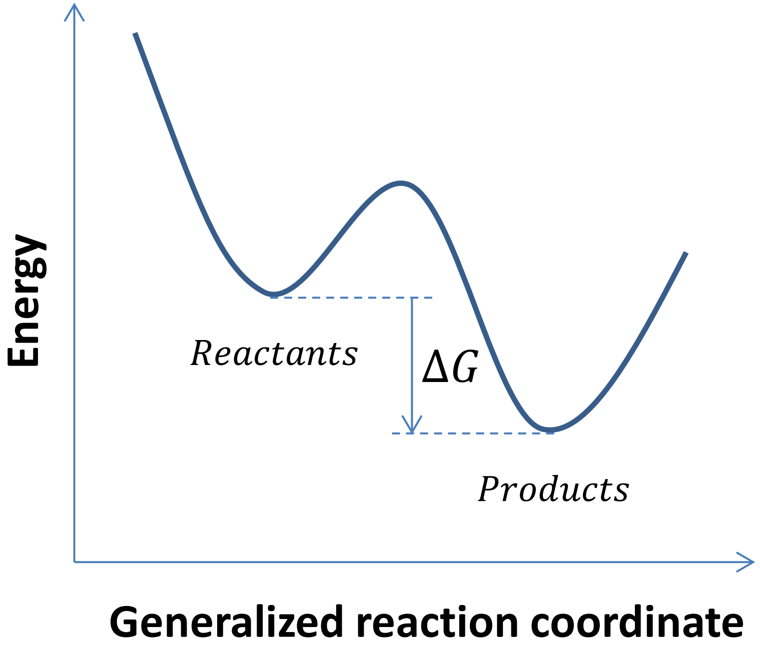
$$\Rightarrow \frac{k_{forward}}{k_{backward}} = \frac{[Products]}{[Reactants]} \equiv K$$ Equilibrium constant

Thermodynamic equilibrium:

$$\Delta G = -RT \cdot lnK$$

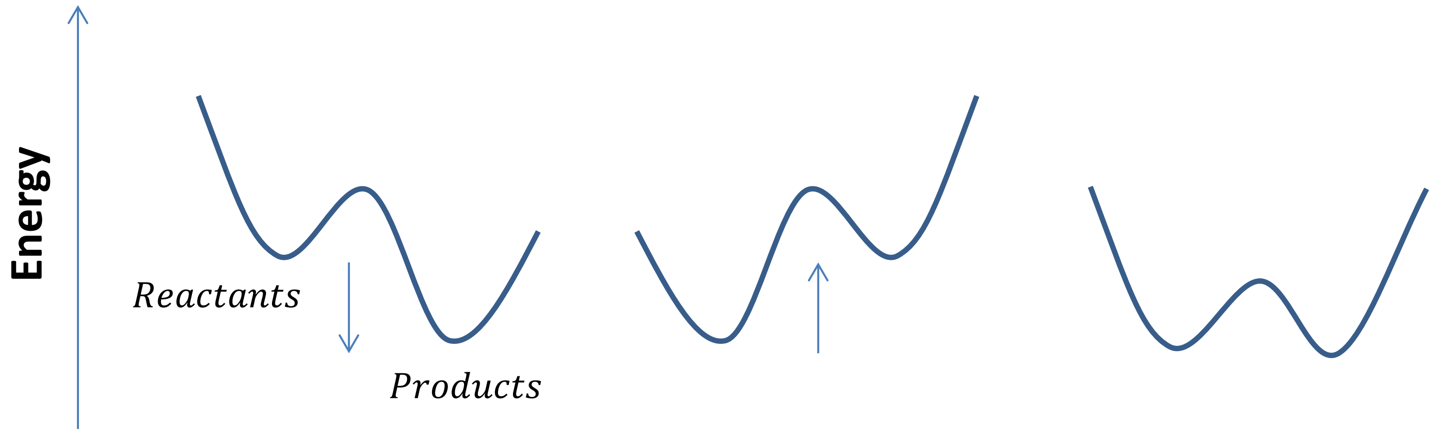
$$\Rightarrow \boxed{K = \frac{[Products]}{[Reactants]} = e^{-\frac{\Delta G}{RT}}}$$

with $\Delta G = G(Products) - G(Reactants)$



Chemical and thermodynamic equilibrium 3

$$K = e^{-\frac{\Delta G}{RT}}$$ with $\Delta G = G(Products) - G(Reactants)$



$\Delta G < 0$
$K \gg 1$

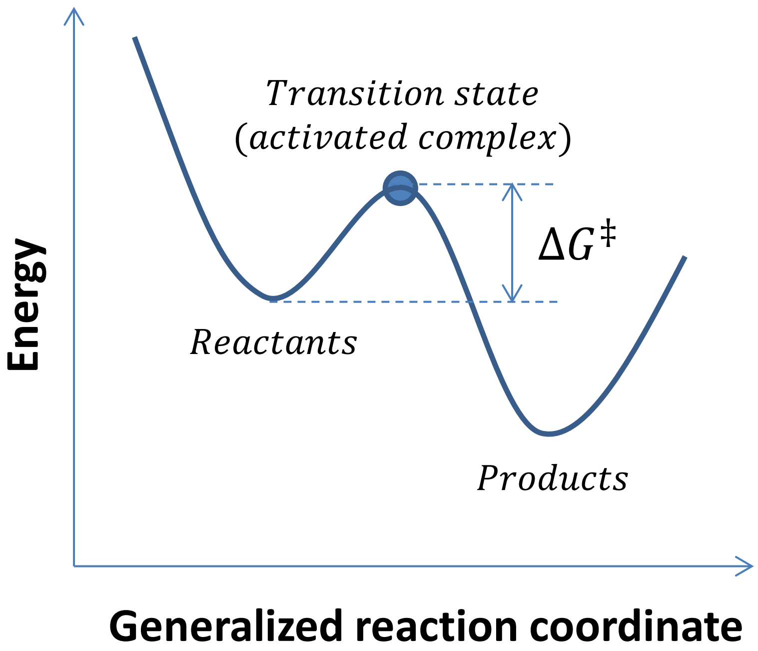
Energy is released

$\Delta G > 0$
$K \gg 1$

Energy is consumed

$\Delta G = 0$
$K = 1$

Transition state theory 1



$$\Delta G^{\ddagger} = G(\mathit{transition\ state}) - G(\mathit{Reactants})$$

$$\mathit{Reactants} \rightleftarrows \mathit{Transition\ state} \;\rightarrow \mathit{Products}$$

$$\mathit{Rate} = \upsilon \cdot [\mathit{Transition\ state}]$$

υ: Crossing frequency (frequency of crossing the barrier)

Collision frequency (for treatment within collision theory)

Neglecting molecular orientation (steric effects)

Transition state theory 2

With $Rate = k \cdot [Reactants]$ it follows:

$\upsilon \cdot [Transition\ state] = k \cdot [Reactants]$

Or

$$\boxed{k = \upsilon \cdot K = \upsilon \cdot \frac{[Transition\ state]}{[Reactants]}}$$

Sometime called the Eyring equation.

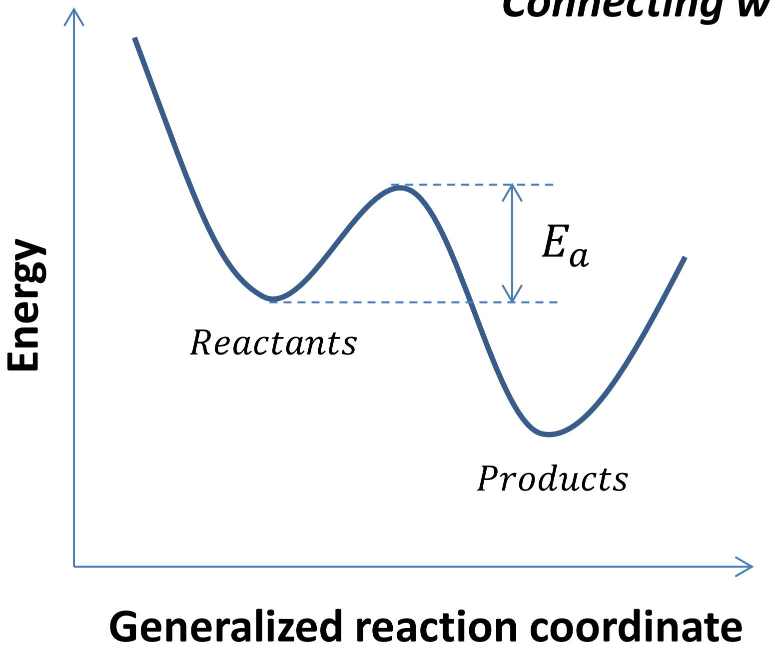
With $K = e^{-\frac{\Delta G^{\ddagger}}{RT}}$ we arrive at:

$$\boxed{k = \upsilon \cdot e^{-\frac{\Delta G^{\ddagger}}{RT}}}$$

Sometime called the Eyring equation.

Transition state theory 3

Connecting with the Arrhenius equation



$$k = A \cdot e^{-\frac{E_a}{RT}}$$

E_a is the activation energy.

What is A (besides an experimental parameter)?

Does A have a physical meaning?

Can E_a be calculated?

Transition state theory gives answers:

- A could be the collision frequency: $A = \upsilon$
- A could be the collosion frequency including a factor ρ accounting for steric effects (such as the relative orientation of molecules): $A = \upsilon \cdot \rho$
- $E_a = \Delta G^{\ddagger}$ can be calculated

Transition state theory 4

Limitations

- Its original goal was to calculate absolute rate konstants („absolute-rate theory“).
- TST turned out to be more successful in calculating the thermodynamic properties of the transition state from measured rate constants (calculating the Gibbs energy $\Delta G^{\ddagger}$ as well as the enthalpy and entropy).
- TST neglects the possibility of tunneling through the barrier (it assumes that the reaction does not occur unless particles collide with enough energy to form the transition structure).
- TST can fail for high temperatures when high vibrational modes are populated and transition states far from the lowest energy saddle point are formed.
- TST assumes that intermediates (reactants and products, see above, of elementary steps in a multi-step reaction) are long-lived (reaching a Boltzmann distribution of energies) and thus TST fails for short-lives intermediates.
- TST generally fails for photochemical reactions (that are determined by the energy potential landscape rather than the thermodynamics properties of TSs).

How big is the “mistake” we make in calculating the energy of a state within the Born-Oppenheimer approximation?

- That’s not an easy question!
- Think about it (slide 11): “Masses of electrons and nuclei are so different (10^4)…”

Within the adiabatic approximation (“electrons follow nuclear motions instantaneously”) we can solve the Schrödinger equation for Ψ_e at fixed R_n repeatedly for many R_n:

$[T_e + V_e]\ \Psi_e(r_e, R_n=\text{const}) = E_e\ \Psi_e(r_e, R_n=\text{const})$ **T_e/V_e = kinetic/potential energy of electrons**

Schrödinger equation with „Produktansatz“:

Mass of elctron m_e

$$\Phi\left\{-\frac{\hbar^2}{\bbox[border:2px solid red]{2m_0}}\Delta-\frac{e^2}{4\pi\varepsilon_0|\boldsymbol{r}-\boldsymbol{R}_1|}-\frac{e^2}{4\pi\varepsilon_0|\boldsymbol{r}-\boldsymbol{R}_2|}\right\}\psi$$

Electrons

$$+\psi\left\{-\frac{\hbar^2}{2m_1}\Delta_1-\frac{\hbar^2}{2m_2}\Delta_2+\frac{e^2}{4\pi\varepsilon_0|\boldsymbol{R}_1-\boldsymbol{R}_2|}\right\}\Phi$$

Nuclei

$$\xcancel{-\frac{\hbar^2}{\bbox[border:2px solid red]{m_1}}(\nabla_1\psi)\nabla_1\Phi-\frac{\hbar^2}{\bbox[border:2px solid red]{m_2}}(\nabla_2\psi)\nabla_2\Phi-\frac{\hbar^2}{\bbox[border:2px solid red]{2m_1}}\Phi\Delta_1\psi-\frac{\hbar^2}{\bbox[border:2px solid red]{2m_2}}}\Phi\Delta_2\psi=E\psi\Phi\,.$$

Neglect within BOA

Masses of nuclei m_n

The neglected part of the energy is smaller by $m_0/m_{1,2} = m_e/m_n = 10^{-4}$

Haken/Wolf *Molecular Physics and Elements of Quantum Chemistry*